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Mine Drainage and Surface Mine Reclamation

Proceedings of a conference sponsored by The American Society for Surface Mining and Reclamation, The Bureau of Mines, and The Office of Surface Mining Reclamation and Enforcement. The conference was held in Pittsburgh, Pennsylvania on April 19-21, 1988.

Volume I: Mine Water and Mine Waste.

MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR

Information Circular 9183

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Volume I: Mine Water and Mine Waste.

Volume II: Mine Reclamation, Abandoned Mine Lands and Policy Issues, is also available from The Bureau of Mines as Information Circular 9184.

UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
David S. Brown, Acting Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

With Factors for Conversion to U.S. Customary Units and the International System of Units (SI)[1]

Abbreviation or unit	Unit of measure	To convert to--	Multiply by--
acre	acre	hectares	0.405
bar	bar	NA	
bu	bushel	NA	
C	coulomb	NA	
cm	centimeter	inches	0.3937
eV	electron volt	NA	
ft	foot	meters	0.3048
ft^2	square foot	square centimeter	929.0
ft^3	cubic foot	cubic meters	0.028
ft/s	foot per second	centimeters per second	30.48
g	gram	ounces	0.0353
gal	gallon	liters	3.785
gal/h	gallon per hour	liters per hour	3.785
gal/min	gallon per minute	liters per minute	3.785
h	hour	NA	
ha	hectare	acres	2.471
in	inch	centimeters	2.54
K	kelvin	NA	
kg	kilogram	pounds	2.205
L	liter	cubic inches	61.025
lb	pound	kilograms	0.4536
lb/min	pounds per minute	kilograms per minute	0.4536
L/min	liter per minute	gallons per minute	0.2642
m	meter	feet	3.28
$\underline{M}$	mole per liter		
$\overline{M}$	mega	NA	
m^3	cubic meter	cubic yards	1.308
m^3/s	cubic meter per second	gallons per second	264.2
mil	mil	inch	0.001 inch
mile	mile	kilometers	1.609
mg	milligram	grains	0.0154
mg/L	milligram per liter	NA	
mg/(L·h)	milligram per liter per hour	NA	
min	minute	NA	
mL	milliliter	cubic inches	0.061
mm	millimeter	inches	0.0394
mmho/m	millimho per meter	NA	
mol	mol	NA	
mol/L	mole per liter	NA	
mV	millivolt	NA	
μm	micrometer	inches	3.94×10^{-5}
ohm	ohm	NA	
pct	percent	NA	
psi	pound per square inch	grams per square centimeter	70.307
std ft^3/min	standard cubic foot per minute	NA NA	
ton	ton	metric tons	0.907
yr	year	NA	

NA Not applicable.

[1] Owing to the preference of individual authors, U.S. customary and SI units have both been used in this report. Conversion factors are provided for the assistance of the reader.

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MINE DRAINAGE AND SURFACE MINE RECLAMATION

Proceedings of a Conference jointly sponsored by the Bureau of Mines, the Office of Surface Mining Reclamation and Enforcement, and the American Society of Surface Mining and Reclamation.

ABSTRACT

Mine waste and mine reclamation are topics of major interest to the mining industry, the government and the general public. This publication and its companion volume are the proceedings of a conference held in Pittsburgh, April 19-21, 1988. There were nine sessions (50 papers) that dealt with the geochemistry, hydrology and problems of mine waste and mine water, especially acid mine drainage. These comprise Volume 1. The nine sessions (43 papers) that dealt with reclamation and restoration of disturbed lands, as well as related policy issues, are included in volume 2. Volume 2 also contains the ten papers that pertained to control of subsidence and mine fires at abandoned mines. Poster session presentations are, in general, represented by abstracts; these have been placed in the back of both volumes.

Reference to companies and specific products in these papers does not imply endorsement by the Bureau of Mines.

USE OF ACID-BASE ACCOUNTS IN PREMINING PREDICTION OF ACID DRAINAGE POTENTIAL: A NEW APPROACH FROM NORTHERN WEST VIRGINIA[1]

Richard S. diPretoro and Henry W. Rauch[2]

Abstract.--Premining prediction of postmining drainage quality is required by law, but the method most often used, involving acid-base accounting, was never intended to predict mine drainage quality and as used in the past has proven unreliable. In this study, postmining drainage chemistry was measured at base flow in a one-time sampling program for 75 surface coal mines in Monongalia and Preston Counties in West Virginia. The drainage chemistry was then compared to available acid-base account parameters to identify reliable premining predictors, if any, of drainage quality. Sampling locations included seeps, springs, first order streams, and inflows to ponds if they primarily contained mine drainage. Each sampling location was paired with the closest available acid-base account log, which was mathematically adjusted to yield the volume percentage of each geochemical unit in the mined coal overburden, plus one foot of pavement. Both total and net neutralization potentials (NP) of overburden are significantly and directly related to net alkalinity (alkalinity minus acidity) of mine drainage. Every sampled mine is producing drainage with positive net alkalinity if it has greater than 40 tons of $CaCO_3$ equivalent of total NP per thousand tons of overburden, or greater than 30 tons of $CaCO_3$ equivalent of net NP per thousand tons of overburden. Conversely, every mine with less than 20 tons per thousand tons of total NP or less than 10 tons per thousand tons of net NP is producing drainage with negative net alkalinity. Total sulfur content and hence maximum potential acidity (MPA) in overburden bears very little relation to mine drainage quality. All mines in this study with very low (<0.2%) sulfur content in overburden produce acid drainage. The ratio of NP to MPA is significantly and directly related to net alkalinity of mine drainage. Every sampled mine is producing drainage with negative net alkalinity if it has an NP to MPA ratio of less than 2.4.

INTRODUCTION

Public Law 95-87 (Surface Mining Control and Reclamation Act 1977) requires premining planning. The law states that surface coal mining permits are not to be issued where required reclamation is not feasible or cannot be accomplished by the plan submitted. Acceptable drainage quality is one of the components of required reclamation and such quality is to be insured in part by pre-identifying acid-producing materials so as to avoid acid drainage. Thus, the Federal government has produced a legal requirement that acid-producing materials in coal overburden and pavement be identified in advance of mining. To aid operators and state agencies in pre-identifying acid-producing materials, the U.S. Environmental Protection Agency (EPA) published a method developed at West Virginia University known as the acid-base account method (Sobek et al. 1978). The method was intended to aid revegetation by identifying the best choices for topsoil substitute material. Although it was not intended by its authors to be used to predict postmining drainage quality, acid-base accounting has been used for that purpose and has produced mixed results (Renton 1985).

---

[1] Paper presented at the 1988 Annual Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U. S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

[2] Richard S. diPretoro is a Consulting Geologist in Morgantown, WV and Henry W. Rauch is a Professor of Geology at West Virginia University, Morgantown, WV.

This study attempted to identify reliable premining predictors of acid drainage potential. This paper reports on reliability of acid-base account parameters for the premining prediction of acid postmining drainage.

Description of the Study Area

The area of study for this project comprises all or part of the areas shown on thirteen 7.5-minute topographic quadrangles of the U.S. Geological Survey in northern Preston and eastern Monongalia Counties, WV (fig. 1).

The coal-bearing rocks are middle Pennsylvanian to Permian in age and consist primarily of sandstone and shale with lesser amounts of limestone and coal. The structures are low-lying open folds trending northeast-southwest.

The climate of the study area is of the humid, continental type characterized by mild summers and cold winters. Rainfall ranges from 42 to 52 inches (Herb et al. 1981). All ground water that is eventually discharged from the study area is generated by the infiltration of precipitation except for minor amounts being flushed from deep saline aquifers.

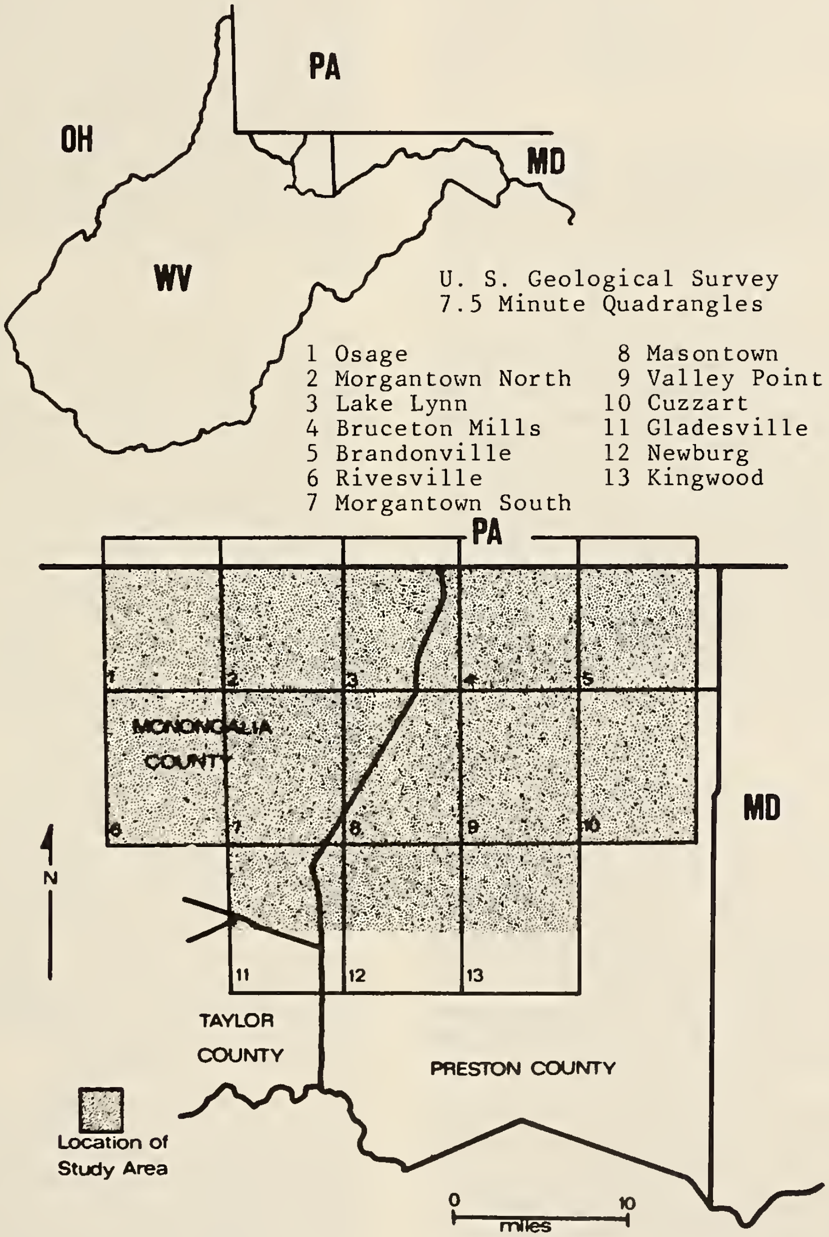
PA
OH
MD
WV
U. S. Geological Survey
7.5 Minute Quadrangles
1 Osage
2 Morgantown North
3 Lake Lynn
4 Bruceton Mills
5 Brandonville
6 Rivesville
7 Morgantown South
8 Masontown
9 Valley Point
10 Cuzzart
11 Gladesville
12 Newburg
13 Kingwood
PA
MONONGALIA COUNTY
MD
N
TAYLOR COUNTY
PRESTON COUNTY
Location of Study Area
0
10
miles
1
2
3
4
5
6
7
8
9
10
11
12
13

Figure 1.--Location map of the study area.

METHODS OF INVESTIGATION

Sampling

Seventy-five surface water sites were selected for a one-time sampling program designed to indicate in a broad sense the quality of drainage from reclaimed surface coal mine sites. The mine sites were selected based on pre-determined criteria discussed below after examining over 400 permit applications for surface coal mines and other water and overburden data at the U.S. Office of Surface Mining Reclamation and Enforcement (OSM) in Morgantown, WVa. All reclaimed surface coal mines in Monongalia and Preston Counties in the Waynesburg, Upper and Lower Freeport, and Upper, Middle, and Lower Kittanning Coal Seams were selected for sampling where the mines could be reached on the ground and had observable drainage. Seventy-five such sites were sampled.

Mine drainage sampling locations included seeps and springs located in and near the mine backfill, both undeveloped and developed for domestic or livestock uses. First order streams and inflows to ponds were also sampled if they primarily contained mine drainage. The selected water sampling sites were usually near vegetated mine backfills that usually had been reclaimed for 2 or more years. They were mostly chosen on the downdip side from the mine drainage source with the highest flow rate. Where possible, they were established at or below the original level of the coal near the center of the mine to increase the chances of discerning any mining effects and to decrease the chances of dilution by unaffected ground water or of complicating effects from other nearby mines. Previously mined areas (before recent mining) were generally avoided, as were mines which had disposed tipple refuse or treatment residues.

The field sites were sampled during base flow (at least 3 days after the last measurable rain), in the spring of 1985. Base flow is not subject to wide fluctuations and is indicative of shallow aquifer ground-water characteristics (Hem 1970, Todd 1980, Helsel 1983). The sampling sites were all located in heavily dissected upland areas not subject to any regional ground-water discharge. Temperature, specific conductance, Eh, pH, and flow rate were measured. Three water samples were collected and treated (as appropriate) for laboratory analysis at each site.

Hot total acidity (HTA), alkalinity, sulfate, total and dissolved iron, and dissolved manganese were determined (for each set of water samples) in the Hydrogeology Laboratory in the Department of Geology and Geography at West Virginia University.

After the drainage sites had been sampled, acid-base accounts from OSM permit files were chosen to be paired where possible with each water sampling point for later comparison. Such logs were taken from the same mine or a mine working the same coal seam within 2 km of the watershed draining to the sampling point. In most cases, logs fell within 1 km of the sampling point watershed as per recommendations of the Suggested Guidelines (Surface Mine Drainage Task Force 1979). Such pairs were created for 30 out of the 75 mines studied.

Adjustment of Core Log Data for Volume

Core logs record the thickness and type of each rock lithology over an area that is so small compared to the area to be mined that they can be considered lines in cross-section. Mined overburden in the field area is not rectangular in cross-section, as it is in Illinois for example, but is more nearly triangular in cross-section because of the notable terrain slopes. Therefore, the volumes of each lithology represented by the core log are not in fact in the same volume proportion to each other in the mined overburden as they are in the linear record of the log. Those near the top are over-represented and those near the bottom are under-represented by an unadjusted log.

Volumetric adjustment is in order if better predictions are to be made of the combined effects that the different overburden rocks will have on water after mine reclamation, assuming that water quality is related to the mass of certain constituents in the rocks. The ideal solution would be to have a closely spaced grid of cores that would be stratigraphically correlated, allowing the strata to be projected to their crop lines according to the dip and strike. The average area of each lithologic unit would then be measured by planimeter and multiplied by its average thickness to arrive at a total volume for each rock lithology. Tonnages would be computed if necessary, based on estimated (or measured) rock densities.

An effort similar to that just described was successfully carried out and described in the literature by Caruccio and Geidel (1981). Such efforts were also carried out for some West Virginia surface mine reclamation permit applications for a brief time in 1981 (diPretoro 1986). The reason for such calculations in permit applications was to compute the amount of limestone that is supposed to be needed to compensate for deficiencies identified by acid-base accounting.

For this study, a simpler volumetric adjustment was designed that could be applied quickly to limited core log data. This volumetric adjustment was conceived by the senior author and carried out by means of a computer program written by Mr. Paul Sutter, systems analyst for the West Virginia University Department of Geology and Geography.

The volumetric adjustment yields the approximate percentage of the total overburden volume occupied by each rock unit and requires knowing only the total thickness of the stratigraphic overburden column, the thickness of the individual rock units, and their relative positions. It starts with the recognition that every mined tract in the field area is part of a slope, hill, or mountain. It assumes that the shape of a mined hill can be approximated as one of a number of three-dimensional shapes, each of which is a triangle in cross-section. These include shapes similar to those for contour mines and area or mountaintop removal mining operations where the top of the mountain is cone or prism shaped (fig. 2). The core log's top is usually located at the highest point of the triangle, and the coal or pavement forms the triangle's base leg which is roughly perpendicular to the core log. Symmetry about the core (vertical axis) is not required on conical shapes, and triangular cross-sections need not be isosceles. (In this study, some logs represented more, or less, overburden than was present at the mine producing the drainage samples. Where the log represented more overburden, the extra amount was removed from the calculations. Where the log represented less overburden, the missing amount could not be evaluated.

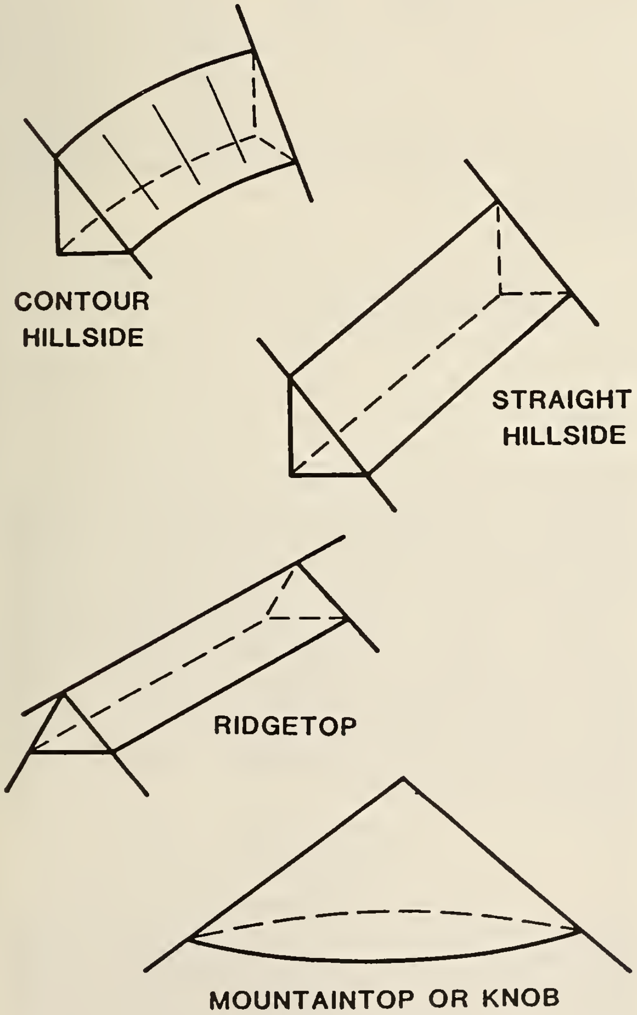

Figure 2.--Idealized shapes of hills having triangular cross-sections when mined.

The program takes the thickness of each layer of rock and calculates the percentage of the area of the whole cross-sectional triangle occupied by that layer. The areas of the triangle and its parts are proportional to the volumes of the corresponding parts of the overburden as a whole (fig. 3).

Because the coal is, for the most part, gone after reclamation, its contribution is removed and the relative percentages of each remaining layer are recalculated. (Bottom coal, partings and other wastes are often left on the pavement but in the interests of simplicity are ignored in this study.) The percentage for each layer is then multiplied as a decimal fraction by the acid-base NP or MPA for that layer to arrive at its contribution to the total for each parameter. The adjusted NP and MPA for each layer is then summed to produce an adjusted NP and MPA for the entire column. Totals of unadjusted NP and MPA are physically meaningless because layer thickness and volume have not been taken into account.

This right triangular method incorporates simplifying assumptions. The core does not always represent all the overburden. The dip is ignored, but the maximum dip is low in the study area, rarely approaching 10 percent. Cross-sections are not exactly triangular, but are slightly elliptical. Lithologic units are usually laterally discontinuous and may thicken, thin or pinch out altogether away from the core hole. Despite its shortcomings, however, the volumetric adjustment technique used in this study is an adequate first approximation and is an improvement over an assumption of a linear relationship between percentage of a certain lithologic unit in a core log and its volume in the mine backfill.

Characterization of Post-Mining Drainage

For the purposes of this study, the legal definition of acid mine drainage (AMD) was used as a basis for characterization of postmining drainage. AMD is legally defined as water discharged from an active, inactive, or abandoned mine and from areas affected by surface mining with a pH of less than 6.0 in which total acidity exceeds total alkalinity (Code of Federal Regulations 1986). The legal definition of acid mine drainage creates an operational parameter to characterize water quality, herein called "net alkalinity," which is calculated by subtracting the acidity from the alkalinity of a drainage water sample with both measured in the same units (mg/L as $CaCO_3$). Net alkalinity can be positive (when alkalinity exceeds acidity) or negative (when acidity exceeds alkalinity). In this study, most drainage samples had only acidity or alkalinity. In the samples that had both acidity and alka-

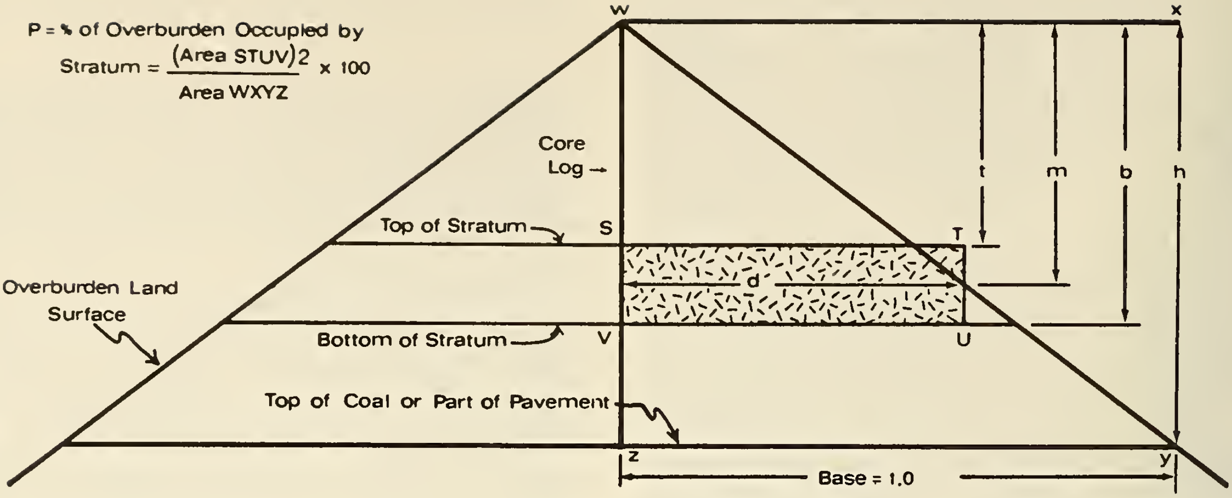
P = % of Overburden Occupied by
Stratum = (Area STUV)2 / Area WXYZ x 100
W
X
Core
Log →
t
m
b
h
Top of Stratum
S
T
d
Overburden Land
Surface
Bottom of Stratum
V
U
Top of Coal or Part of Pavement
Z
Y
Base = 1.0

Figure 3.--Triangular cross-sections of idealized hill, showing variables used in the volumetric adjustment program.

linity, one outweighed the other by a factor of at least 10 in most cases.

Net alkalinity for the sampled drainage sites was compared by use of graphical data plots and statistical analyses with values for the geochemical parameters evaluated. All the raw data were reported by diPretoro (1986); diPretoro and Rauch (1987) reported other results of the same study having to do with lithologic parameters.

RESULTS AND DISCUSSION

In spite of their shortcomings, acid-base accounts were used in this study because they are available in large quantity and they do give some useful information on the geochemical nature of the individual strata.

Neutralization Potential (NP) and Net NP

Figure 4 compares net alkalinity of mine drainage to the acid-base account parameter of net NP in overburden, with each plotted point representing a sampled mine site. The statistically significant regression line depicts the average rise of net alkalinity of drainage with increasing net NP. Figure 4 also shows that all sites having net NP of less than 10 tons of calcium carbonate equivalent per thousand tons of overburden had drainage with negative net alkalinity, while all sites having net NP of greater than 30 tons per thousand had drainage with positive net alkalinity. Note that the acid-base account method defines potentially toxic material in individual strata as that having a net NP of less than -5 (Sobek et al. 1978). This study indicates that the threshold level of concern for net NP for the overburden as a whole must be set higher. A similar trend (with a slightly lower R value that is statistically significant at 0.05 alpha) was also observed for total NP. All sites with total NP greater than 40 tons per thousand tons had drainage with positive net alkalinity while all sites with less than 20 tons per thousand tons had drainage with negative net alkalinity.

Maximum Potential Acidity (MPA)

MPA, calculated by multiplying total sulfur content as a decimal fraction by 31.25 (Sobek et al. 1978, p. 55), was found to have no statistically significant relationship (at 0.05 alpha) to net alkalinity of mine drainage. As shown in figure 5, there appears to be a slight rise in average net alkalinity with rising sulfur content, and all sites with very low sulfur produce acid. This seeming anomaly relates to the NP/MPA ratio present. NP of overburden rises as MPA rises, but NP rises at a faster rate. Very low MPA values are on average associated with proportionately less NP (and hence neutralizing capability) than are higher MPA values (above 5). The median value of NP/MPA ratio for sites in this study with MPA below 5 is 0.5. The median value of NP/MPA ratio for sites with MPA above 5 is 2.9.

NP/MPA RATIO

Caruccio et al. (1980) and Caruccio and Caruccio (1982) have found a strong relationship between drainage quality and carbonate to sulfur ratio. In this study, the ratio of NP to MPA (herein called RATIO) was assumed to approximate the ratio of carbonate to sulfur. The regression line showing the relationship of RATIO to net alkalinity in mine drainage had the

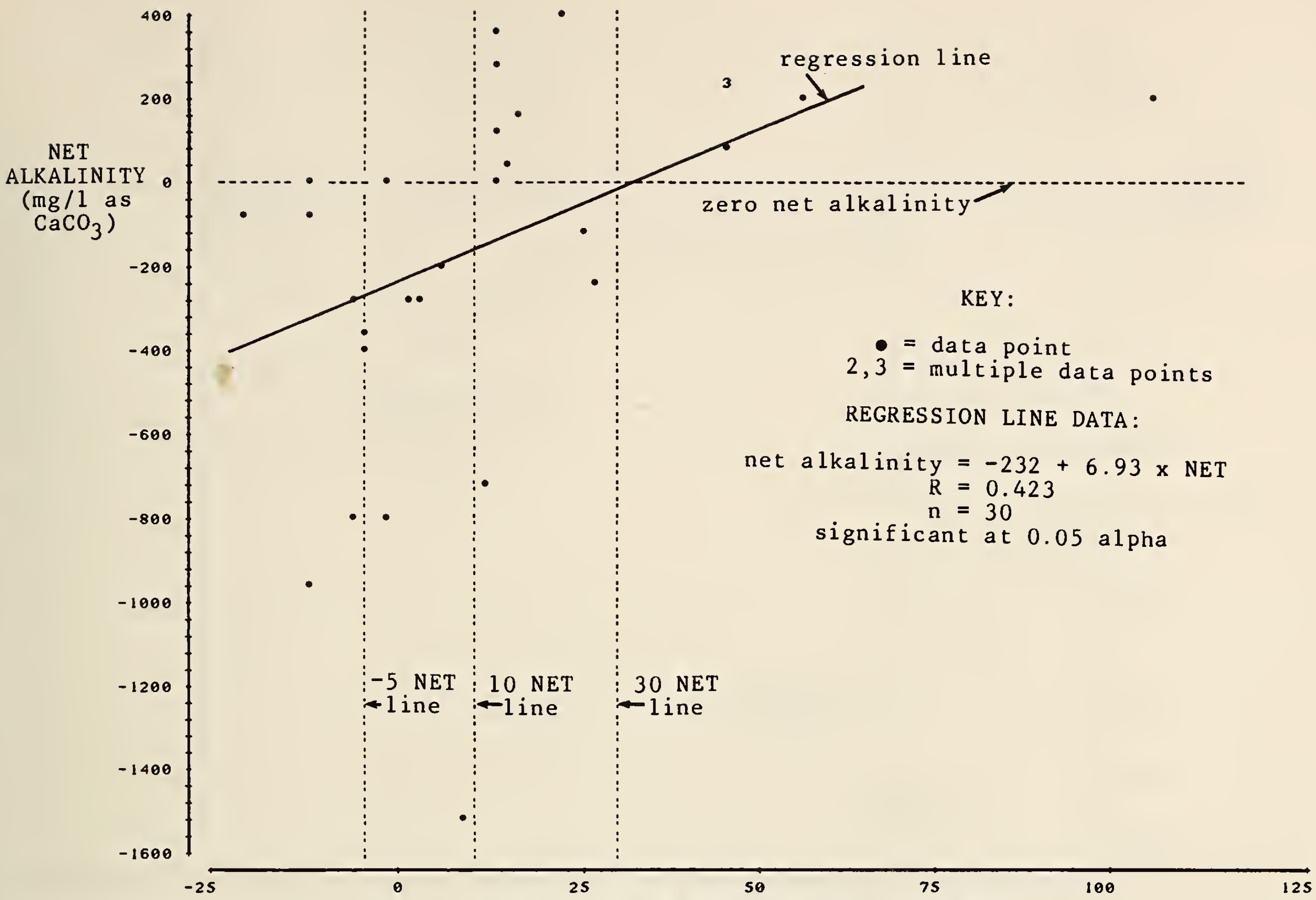

Figure 4.--Net alkalinity in mine drainage versus acid-base net neutralization potential in coal overburden.

greatest degree of statistical significance of those for the acid-base account parameters tested in this study. Figure 6 shows that all of 15 sites having a RATIO of less than about 2.4 had drainage with negative net alkalinity, while 11 of 14 sites having RATIOs greater than about 2.4 had drainage with positive net alkalinity. Note that the presently used acid-base account method would place the critical RATIO boundary below 1.0 (or even below zero) because geologic units having net NP greater than -5 are considered not potentially toxic (Sobek et al. 1978, Surface Mine Drainage Task Force 1979, Erickson et al. 1985). For example, one acid-base account in this study has an NP of 0.3 and an MPA of 4.6, producing a RATIO of 0.1. Strict application of acid-base account guidelines would result in this overburden being considered by some persons not potentially toxic because 0.3 minus 4.6 is greater than -5.0. The drainage from the two sampling locations within 2 km of this acid-base account, however, is highly acid.

CONCLUSIONS

This investigation of reclaimed surface coal mine sites in the northern West Virginia study area has led to four conclusions about the study results and a fifth general conclusion about acid-base accounting:

1) After adjusting acid-base account core logs for volume, all sites with acid-base neutralization potential (NP) greater than 40 tons per thousand tons of overburden equivalent calcium carbonate yield drainage having positive net alkalinity; all sites with NP less than 20 tons per thousand tons equivalent calcium carbonate yield drainage having negative net alkalinity.

2) Acid-base maximum potential acidity (MPA, calculated by multiplying percentage sulfur by 31.25) in premining coal overburden bears very little relation to net alkalinity of post-mining drainage in the study area except that below about 0.2 percent sulfur, reclaimed overburden is likely to produce acid drainage because of concomitant low neutralizing capacity.

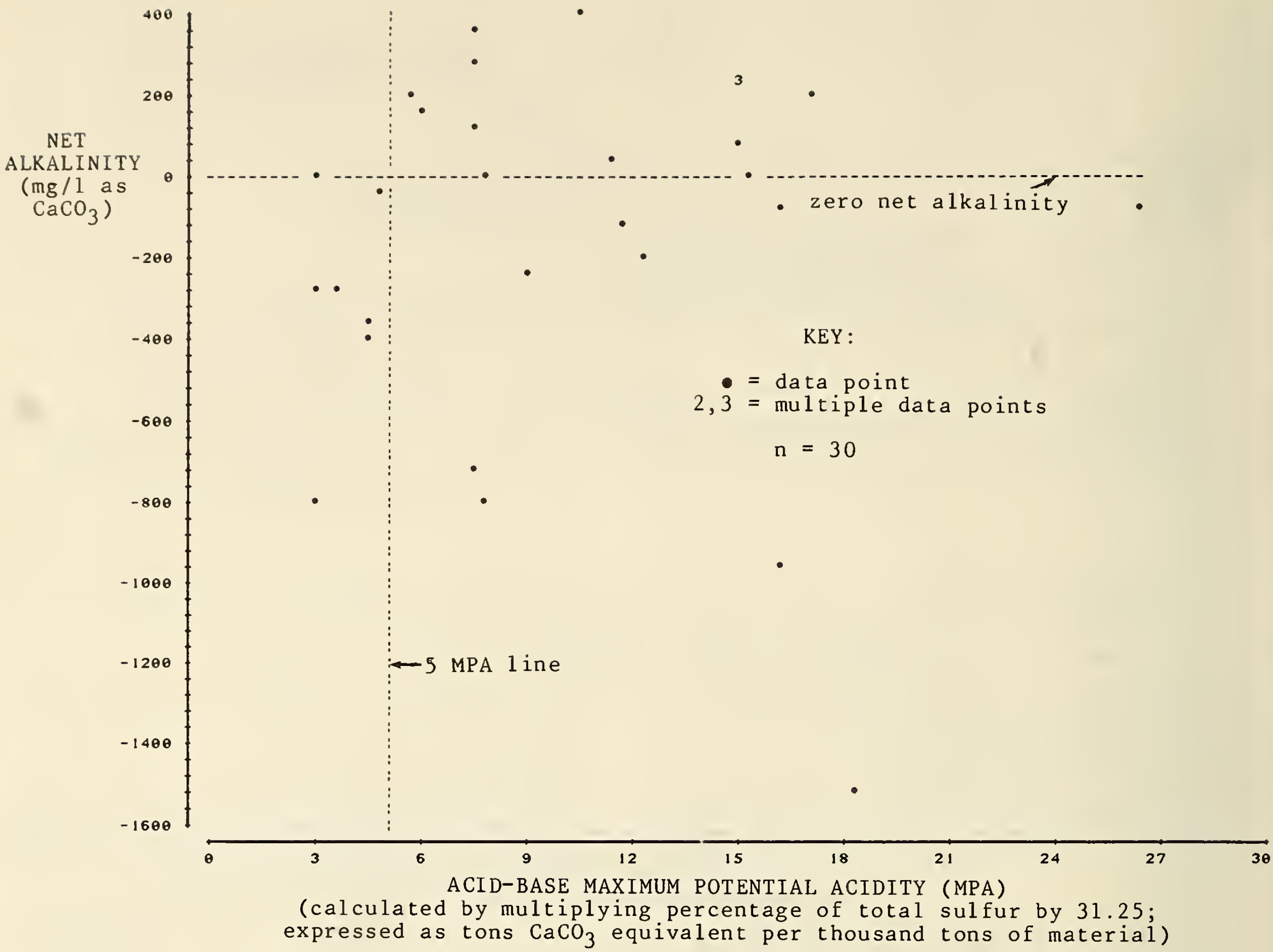

Figure 5.--Net alkalinity in mine drainage versus acid-base maximum potential acidity in coal overburden.

3) All sites with acid-base net NP (NP-MPA) greater than 30 tons per thousand tons of equivalent calcium carbonate (20 percent of sites in this study) yield drainage having positive net alkalinity; all sites with net NP less than 10 tons per thousand tons calcium carbonate equivalent (47 percent of sites in this study) yield drainage having negative net alkalinity. The original acid-base account application, which placed the threshold level of net NP for drainage having positive net alkalinity at -5 (same units), was obviously in error.

4) Acid-base NP divided by MPA yields a variable called RATIO. Sites with RATIO values greater than 2.4 are most likely to produce drainage having positive net alkalinity; sites with RATIO less than 2.4 are most likely to produce drainage having negative net alkalinity. The original acid-base account application which placed the threshold level of RATIO for drainage having positive net alkalinity at or below 1.0, was in error.

5) Despite its limitations, acid-base accounting can be used more effectively than it is currently being used to produce accurate premining assessments of postmining drainage quality. Because of the complexity of coal mining and reclamation operations, professional judgement (taking into account lithology and history of drainage quality in a given area, as well as acid-base account parameters) will always be required to arrive at a final determination.

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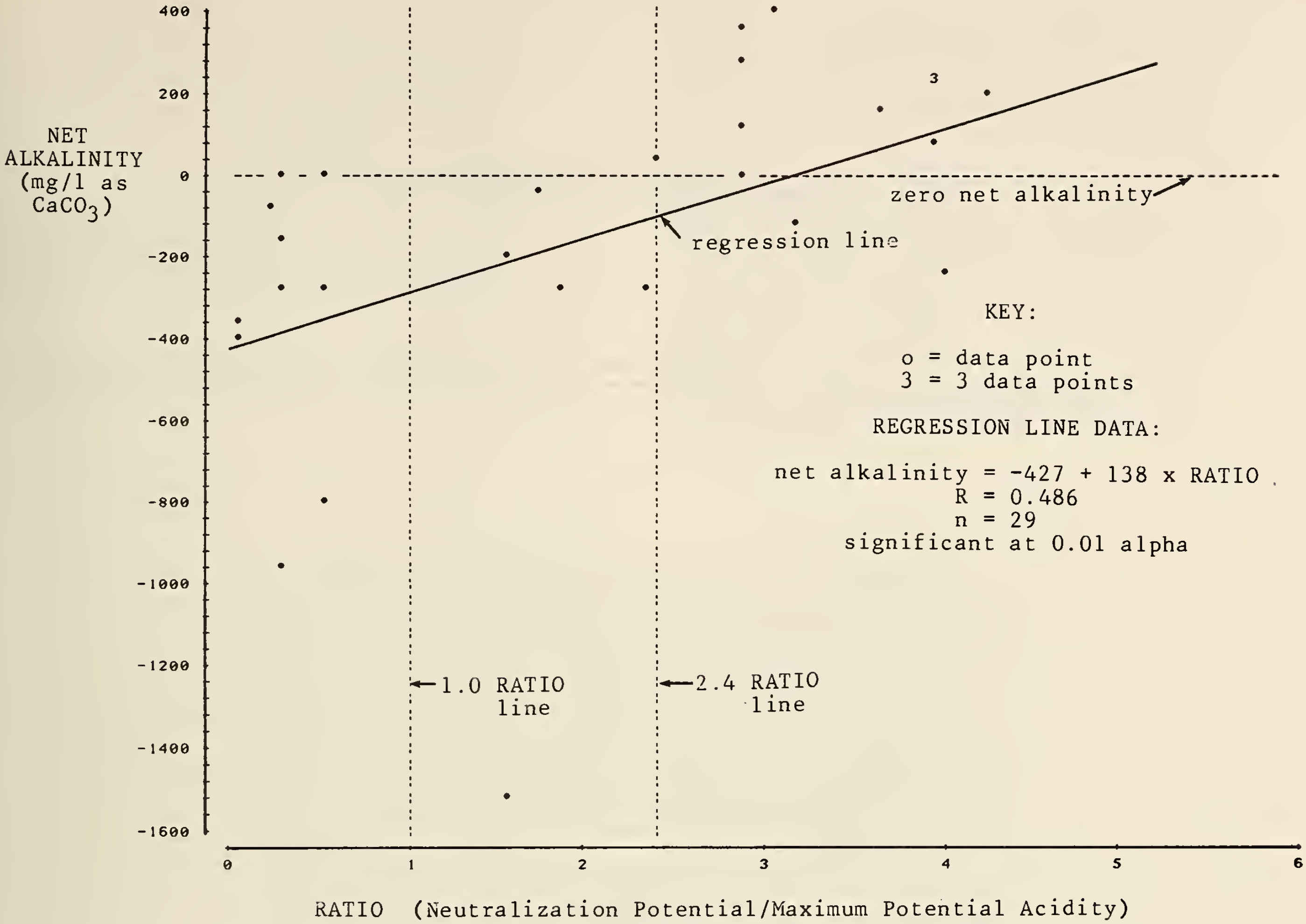

Figure 6.--Net alkalinity in mine drainage versus acid-base account RATIO (NP/MPA) in coal overburden.

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EVALUATION OF OVERBURDEN ANALYTICAL METHODS AS MEANS TO PREDICT POST-MINING COAL MINE DRAINAGE QUALITY[1]

Patricia M. Erickson and Robert S. Hedin[2]

Abstract.--Prediction of the potential for acid drainage formation is required as part of the coal mine permitting process. Overburden analyses, by methods such as the acid-base account, are in common usage as part of this prediction despite the fact that a quantitative correlation between overburden properties and post-mining water quality had never been demonstrated adequately in the field. This study was designed to test the accuracy of predictions based solely on overburden analytical data. The study sites were selected to represent cases that have proven difficult to predict. Overburden samples were obtained from freshly exposed surfaces on highwalls or from cores preserved prior to mining. Post-mining drainage was analyzed at a reclaimed section of each site, paired to match the sampled overburden in terms of the presence and thickness of lithologic units. Overburden samples were analyzed by the acid-base account and a simulated weathering method. Overburden data were aggregated on thickness- and volume-weighted bases and water quality data were aggregated on a flow-weighted basis for each site. Drainage net alkalinity was correlated significantly ($p<0.05$) with the volume-weighted acid-base account parameters acid potential, neutralization potential, and net neutralization potential ($r=0.358$, 0.4197, 0.3799, respectively). However, when five sites having net neutralization potentials greater than 20 tons/1000 tons were excluded, these relationships became insignificant. Acid base account data showed boundaries useful in predicting the acid or alkaline character of post-mining drainage but no quantitative predictive equation could be developed. Simulated weathering test data correlated with actual sulfate concentrations in the post-mining seeps ($r=0.4089$, $p=0.046$), but the alkaline or acid nature of the seeps was not correlated with laboratory data ($r=0.088$, $p=0.364$).

INTRODUCTION

Overburden analysis came into widespread use with passage of the Surface Mining Control and Reclamation Act of 1977 (Public Law 95-87). The law requires, as part of the permitting process, the identification of potentially acid-producing strata and determination of the probable hydrologic consequences of mining, including water resource degradation. Because little research had been conducted on water quality prediction, the regulatory authorities and industry initially had to adapt available methods to these purposes.

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The acid-base account method of overburden analysis was developed in the early 1970's for identification of strata that could be used as soil substitutes in revegetation of coal mines (Smith et al 1974). The method (described subsequently in this paper) is based on determining whether the capacity of a stratum to produce acid via pyrite oxidation is greater or less than the ability of the same stratum to neutralize strong acid. A neutralizer deficiency greater than 5 tons/1000 tons as calcium carbonate equivalent[3], a figure common for natural soils in West Virginia, was the recommended standard for identifying strata unsuited for supporting vegetation.

This method was adopted widely as the overburden analytical tool for identification of acid and toxic strata. The term "toxic" was meant to indicate toxic to plants by virtue of high acidity levels. While the purpose and application of the method was delineated clearly in the literature, its more recent use as an indicator of water quality is not clearly defined.

Based on the real or perceived failure of the acid-base account to identify acid-producing strata and predict whether or not post-mining discharges would comply with regulatory standards, interest in other overburden analysis methods has grown. The numerous alternative methods can be classified as static or kinetic; the former rely on bulk rock properties while the latter take into account the rates of relevant reactions. Simulated weathering tests are kinetic methods that aim to accelerate in the laboratory the reactions that take place in the field setting. Common static and kinetic tests have recently been reviewed (Ferguson and Erickson, 1987).

At the start of this study, none of these methods had been adequately evaluated by comparing the predicted water chemistry to actual drainage chemistry. That is, there was no procedure for interpreting the results to predict post-mining water quality or character with a known degree of accuracy. The purpose of this study was to define the predictive capability of overburden analytical methods by applying them to many mine sites. Post-mining water quality measurements were made at the discharge points from reclaimed mine sections. Pre-mining overburden samples were collected from preserved cores or from fresh channels cut in extant highwalls. These samples were analyzed using the acid-base account method and a simulated weathering test. The results of both overburden tests were then compared with the water quality results to determine if significant correlations exist.

METHODS

Technical Approach

Thirty-two sites were selected for the study, each comprised of a pre-mining section and a post-mining reclaimed section, so that pre- and post-mining data could be gathered simultaneously. The general concept was developed at the Bureau of Mines while the detailed approach was developed by Engineers International in response to our request for proposals. The contractor and its subcontractor, Sturm Environmental Services, selected all sites, conducted all sample collection and performed all water and rock analyses. Bureau personnel conducted all data analysis following completion of the contract.

Sites were selected to represent cases that are difficult to predict. Overburden columns completely dominated by either acidic or alkaline strata were eliminated from consideration. Sites that were backfilled or reclaimed using acid-mitigating methods, such as selective spoil placement or surface alkaline addition, were also excluded. To minimize effects of local geology, sites in Pennsylvania, West Virginia, Maryland, Illinois and Kentucky were included in the study. Sites in west-central and southwestern Pennsylvania comprised about half of the study sites, through a prevalence of suitable candidates rather than through design.

Water Quality

Sampling and Analysis

Post-mining water quality data were collected from reclaimed spoil sections at 32 mine sites paired with overburden sampling sites. Water sampling and flow measurement were conducted at all discharge points identified during the initial visit to each site. The discharges that comprised the majority of the flow, usually two or three at each site, were sampled subsequently at least nine times over about a year. Primary measurement and analysis methods for parameters used in this report are shown in Table 1.

Table 1.--Analytical methods for selected parameters (U.S. EPA 1983)

Parameter	Measurement Method
Water flow........	Bucket and stopwatch, L/min
pH................	Electrometric, standard units
Acidity...........	Titration (hot, peroxide) to pH 8.3, mg/L as $CaCO_3$
Alkalinity........	Titration (cold) to pH 4.5, mg/L as $CaCO_3$
Net Alkalinity....	Alkalinity minus Acidity, mg/L
Sulfate...........	Colorimetric methyl thymol blue, mg/L

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[3] The unit, tons/1000 tons, derives from agronomy where 1000 tons is the estimated weight of an acre-plow layer of soil. The unit is identical to parts per thousand. $CaCO_3$ equivalent indicates the mass of calcium carbonate needed to yield a specific magnitude of electrical charge ($CaCO_3$ = 50 g/mol of charge). The unit is used so that terms of opposite charge, such as acidity and alkalinity, are additive.

Data Aggregation

Water quality data for each site were aggregated to produce a single value for each parameter by calculating a flow-weighted average:

$$\text{flow-weighted } X = \frac{\sum_{1}^{n} (\text{concentration of } X)(\text{flow})}{\sum_{1}^{n} (\text{flow})} \qquad (1)$$

where n is the total number of samples at the site for which flow and concentration of X were measured and X is the chemical quantity net alkalinity, sulfate, or iron in mg/L.

Overburden

Sample Collection

Overburden samples were collected in two ways to represent pre-mining conditions. At nine sites, well-preserved and well-documented core samples taken prior to mining of the reclaimed section of the site were used for analysis. In all other cases, a highwall that could be determined to match the backfill, in terms of the presence, thickness, and appearance of each lithologic unit, was sampled for overburden analysis. Highwall samples were collected from a channel of freshly exposed surfaces, with lateral displacement at lithologic boundaries where needed to represent the stratum as records showed it had existed in the reclaimed section prior to mining. The entire length of each lithologic unit was sampled to account for intra-stratum differences in composition. An average of eight rock units (individual strata or adjacent strata of similar appearance) were collected from each site.

Acid-base Account

Acid-base account analyses were conducted according to procedures developed at West Virginia University (Smith et al 1974, Sobek et al 1978) with minor modifications. The portion of the procedure that produced data used in this paper is as follows. Samples were air-dried, mixed, crushed to pass a 60-mesh sieve, and stored in sealed containers until analyzed.

Acid potential (AP) is defined as the amount of acid that would be produced if all pyrite in the sample reacted according to the following stoichiometry:

$$FeS_2 + \frac{15}{4}O_2 + \frac{1}{2}H_2O = Fe(OH)_{3(s)} + 2SO_4^{2-} + 4H^+ \qquad (2)$$

One mole of pyrite, containing 64 g sulfur, produces 4 moles of H^+ acidity, equivalent to 200 g $CaCO_3$ acidity. Thus, the acid potential of pyritic sulfur is 3.125 g acidity (as $CaCO_3$) per g sulfur; 1 pct pyritic sulfur has the potential to produce 31.25 tons/1000 tons acidity. Total sulfur concentrations were measured with an automated Fisher sulfur analyzer, consisting of a furnace and SO_2 titrator, according to the instrument instructions. Sulfur speciation was analyzed for samples containing more than 0.5 pct sulfur by hot extraction with hydrochloric and nitric acid to remove sulfate and pyritic sulfur, respectively. Organic sulfur was defined as the sulfur fraction remaining after acid extraction. AP was calculated from both total sulfur and, when analyses were available, pyritic sulfur. Total sulfur is often used in mine permit applications to minimize analytical costs.

Neutralization potential (NP), defined as the ability of the stratum to neutralize strong acid, was determined by treating a 2 g sample with 20 to 80 mL of 0.1 $\underline{M}$ HCl, heating nearly to boiling, and swirling periodically until no gas evolution was observed. The samples were made up to 125 mL with distilled water, boiled for 1 min, and cooled to room temperature. The treated sample was then titrated with standard NaOH (0.1 or 0.5 $\underline{M}$) to pH 7. NP was calculated as the amount of HCl consumed by the sample and converted to the units of tons $CaCO_3$/1000 tons material:

$$\text{NP, tons/1000 tons} = \frac{\text{g HCl consumed}}{\text{g sample}} \times \frac{50 \text{ g } CaCO_3}{36 \text{ g HCl}} \times 1000 \qquad (3)$$

Net neutralization potential (NETNP) was calculated for the stratum by subtracting AP from NP. A positive NETNP indicates an excess of neutralizers while a negative NETNP indicates a deficiency of neutralizers in the stratum.

Simulated Weathering

A simulated weathering procedure was applied to all samples from 18 of the 32 study sites. The subset of sites, necessary to save cost, was selected to cover the range of post-mining water quality observed at all sites and to include sites for which true water quality and acid-base account results conflicted.

Samples were crushed to pass a 2-mm sieve and 300 g portions were placed in a thin layer on the bottom of weathering chambers. The chambers were each rinsed with 300 mL of distilled water; the collected leachate was labelled "week 1" and analyzed. An inoculant of 10 mL of acid mine drainage was then added to each sample to establish a population of iron-oxidizing bacteria. For the next 5 to 8 weeks, leaching was performed on a 7-day cycle: dry air was passed over the sample for 3 days; humidified air was passed over the sample for 3 days, and leaching occurred on the last day, by the addition of 300 mL of distilled water for 1 hr followed by draining. Any fines washed out during draining were collected by centrifugation, resuspended in a small amount of water, and returned to the chamber. The leachate volume was measured and portions were analyzed for pH, acidity, alkalinity, iron, and sulfate (table 1).

Leachate composition from each sample was aggregated over the duration of the weathering test to calculate cumulative loads of pollutants. Cumulative load of net alkalinity (alkalinity minus acidity) was calculated according to:

$$\text{Cumulative net alkalinity, mg} = \sum_{2}^{n} \left[(\text{net alkalinity, mg/L})(\text{leachate volume, L})\right] \qquad (4)$$

where n is the total number of weeks of leaching. Cumulative sulfate load was calculated in the same manner.

The same simulated weathering procedure was also applied to composite samples from 5 of the study sites. Composite samples were made by mixing all the strata from a site in weight ratios equal to the thickness ratios of the strata in the overburden column. Equation (4) was again used to calculate cumulative product loads.

Data Aggregation

Overburden analytical data from both the acid-base account and single-stratum simulated weathering tests were aggregated in two ways to produce a single value to represent the entire overburden column at each mine. First, a thickness-weighted average was calculated as

thickness-weighted NETNP =

$$\frac{\sum_{1}^{n}[(\text{NETNP})(\text{thickness})]}{\sum_{1}^{n}(\text{thickness})} \qquad (5)$$

where n is the total number of strata sampled at the site.

Second, a volume-weighted average, modelled after diPretorio's (1986), was calculated by substituting an estimated volume for thickness in the previous calculation. The volume of each unit was estimated by assuming that the mine cross-section was an isoceles right triangle, having two sides equal to the height of the overburden column. Using geometry, these assumptions yield the cross-sectional area of a stratum:

$$\text{Area} = 1/2\ (D_2^{2} - D_1^{2}) \qquad (6)$$

where D_1 and D_2 are the depths of the top and bottom of the stratum, respectively.

Assuming constant length and constant density for all strata, the proportion of spoil produced from an individual overburden unit was calculated as:

$$\text{Fractional Volume} = \frac{D_2^{2} - D_1^{2}}{D_T^{2}} \qquad (7)$$

where D_T is the total depth to coal.

Data Analysis

Data were entered and manipulated in Fortran-readable files on a VAX mainframe computer. Descriptive statistics, Pearson correlations and linear regression analyses were performed using SPSS-X software. The significance of correlations was judged at the 0.05 probability level.

RESULTS AND DISCUSSION

Water Quality

Descriptive statistics for selected water quality data are summarized at the individual sample and mine levels in Table 2. Samples collected from a single site often showed changes in water quality during the study period. Many sites had seeps of both acidic and alkaline drainage (fig. 1), and individual seeps occasionally changed character during the study period (fig. 2). Peak contaminant concentrations and loads occurred at different times of the year in different seeps (fig. 2). These observations are a reflection of the heterogeneity of both the spoil material and its local environment within the backfill (Ladwig and Campion; Lusardi and Erickson). They also illustrate the difficulty associated with using aggregated values to represent the entire mine site. However, as drainage from a site usually flowed into one water course, it seemed reasonable to attempt to weight the water quality parameters by flow to represent the site discharge.

Mean and median values of net alkalinity, iron, and sulfate were not in accordance with the stoichiometry shown in equation (2). Equation (2) produces 25 parts net acidity (or 25 parts net alkalinity) per 24 parts sulfate and no dissolved iron. Different stoichiometric equations describe pyrite oxidation at the low pH values that were observed at several sites:

$$FeS_2 + 14Fe^{3+} + \frac{1}{4}O_2 + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^{+} \qquad (8)$$

$$14Fe^{2+} + \frac{14}{4}O_2 + 14H^{+} = 14Fe^{3+} + 7H_2O \qquad (9)$$

$$FeS_2 + \frac{15}{4}O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^{+} \qquad (10)$$

Equations 10 and 2 yield the same ratio of acidity to sulfate (2 moles H^+ acidity and 2 moles latent H^+ acidity in the Fe^{2+} produced in equation 10 versus 4 moles H^+ acidity in equation 2). Equation 10 produces 25 parts net acidity and 7 parts iron per 24 parts sulfate.

Neutralization of pyrite oxidation products by carbonate minerals (e.g., $CaCO_3 + 2H^+ \longrightarrow Ca^{2+} + H_2O + CO_2(g)$) can decrease acidity relative to sulfate in the drainage. The accompanying rise in pH causes iron hydrolosis and precipitation. Only drainage from highly pyritic and neutralizer-free wastes, such as aged coal refuse, approaches the stoichiometry expected from equation (10).

Table 2.—Descriptive statistics for selected post-mining water quality variables.[1]

Parameter	Mean	Median	Range
All individual samples (n = 797)			
Net alkalinity, mg/L as $CaCO_3$.....	-109.	13.0	-2620. - 620.
Iron, mg/L........................	14.1	2.68	0.00 - 99.0
Sulfate, mg/L.....................	1090.	805.	23.0 - 4350.
Flow-weighted mine aggregate			
Net alkalinity, mg/L as $CaCO_3$.....	-130.	-30.6	-1630. - 536.
Iron, mg/L........................	10.9	4.43	0.034 - 50.1
Sulfate, mg/L.....................	1140.	826.	37.4 - 4020.

[1] Values rounded to 3 significant figures.

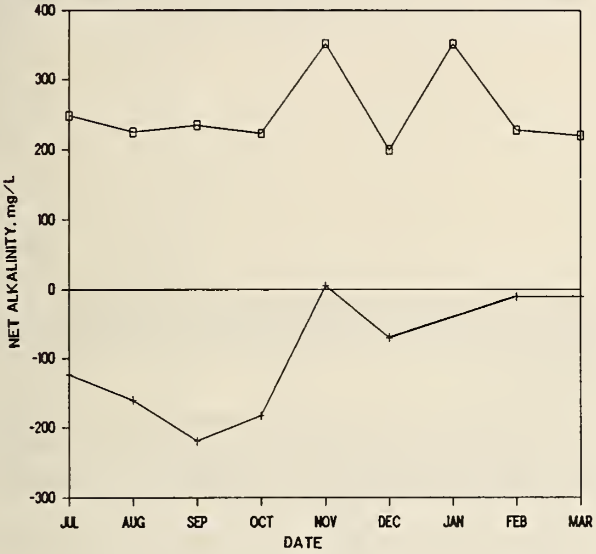

Figure 1.--The major seeps at site 21 discharged both acid and alkaline water.

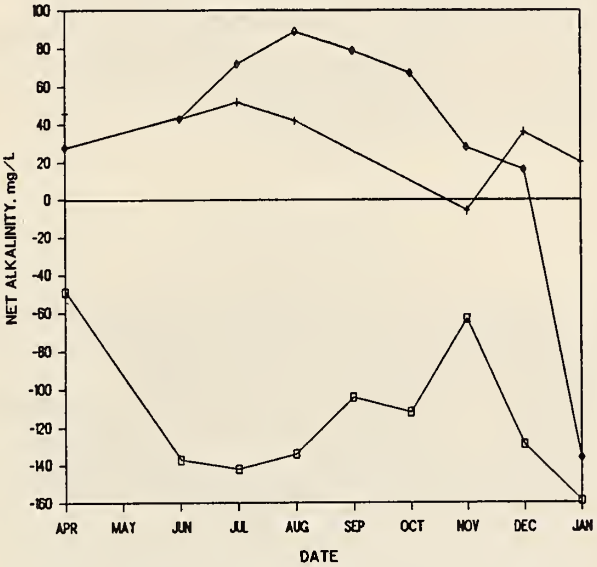

Figure 2.--Seep alkalinity at site 4 varied laterally and temporally.

Carbonate minerals in equilibrium with clean water at atmospheric pCO_2 are expected to yield less than 100 mg/L net alkalinity. Yet alkalinities measured at several sites in this study were higher, with a maximum of 620 mg/L (Table 2). Elevated pCO_2, possibly produced by acid dissolution of limestone, increases the solubility of carbonate minerals. Elevated pCO_2 levels have been measured in acidic coal mine spoil.

Aggregated at the mine level, net alkalinity ranged from -1630 to +536 mg/L, while mean sulfate concentrations ranged from 37.4 to 4020 mg/L (table 2). Seventeen of thirty-two sites produced acidic drainage. These values indicate that the site selection methods were adequate to identify mines that produced drainage of both acceptable and unacceptable quality.

Table 3.--Descriptive statistics for acid-base accounts.[1,2]

Parameter	Mean	Median	Range
All samples			
AP[2].............	21.6	5.84	0.031 - 258.
NP.............	37.6	8.41	0.22 - 937.
NETNP...........	15.8	1.77	-257. - 936.
Thickness-weighted mine aggregates			
AP.............	11.8	9.36	1.04 - 34.2
NP.............	38.1	13.4	3.43 - 272.
NETNP...........	26.2	5.81	-22.7 - 252.
Volume-weighted mine aggregates[3]			
AP.............	17.4	14.3	1.57 - 51.8
NP.............	39.1	15.3	3.30 - 197.
NETNP...........	21.6	4.01	-31.6 - 157.

[1] All values rounded to 3 significant figures or 2 decimal places.

[2] Total sulfur values that registered below the detection limit were recorded as 0.001 pct, giving rise to a single-stratum AP value of 0.031.

[3] Site 13 was omitted since insufficient data were available to estimate volumes.

Table 4.--Correlation between flow-weighted water quality parameters and overburden variables derived from acid-base account data.

	Water Variables Correlation coefficients (probability)	
Overburden variables, tons/1000 tons	Flow-weighted net alkalinity mg/L as $CaCO_3$	Flow-weighted sulfate mg/L as SO_4
Thickness-weighted		
AP.............	0.3050 (0.045)	0.1655 (0.183)
NP.............	0.2562 (0.078)	0.2785 (0.061)
NETNP...........	0.2225 (0.110)	0.2672 (0.070)
NP/AP...........	0.0701 (0.352)	0.2001 (0.136)
Volume-weighted		
AP.............	0.3580 (0.024)	0.0845 (0.326)
NP.............	0.4197 (0.009)	0.3701 (0.020)
NETNP...........	0.3799 (0.018)	0.3866 (0.016)
NP/AP...........	0.2096 (0.129)	0.2986 (0.051)

Acid Base Account

Net neutralization potential (NETNP, equal to the neutralization potential less the acid potential) was calculated for each overburden unit from each site using total sulfur data. Descriptive statistics are shown in Table 3. A wide range of acid-base properties were exhibited in the data set. Eighty-five of 264 individual strata were potential acid-producers according to the 5 ton/1000 ton neutralization deficit (NETNP<-5 tons/1000 tons) used for revegetation. Every site had at least one rock unit that met this criterion for acid potential, yet only 17 of the sites produced acidic drainage. Therefore, the presence of a stratum having NETNP<-5 tons/1000 tons was not a useful means to predict acidic drainage.

Post-mining alkalinity and sulfate concentrations were correlated with several acid-base account parameters (Table 4). The correlations generally were stronger when the acid base account values were aggregated by overburden volume rather than thickness. This is expected because the strata are represented more truly in the former aggregation even though the mine geometry assumptions were crude. Volume-weighted AP, NP, and NETNP were all significantly related to drainage net alkalinity, while only NP and NETNP were significantly related to drainage sulfate. Even when AP was calculated from pyritic sulfur values the correlation was not significant at the 5 pct level (unpublished data from this study). There was only a marginally significant relationship between sulfate concentration in the drainage and the value of NP/AP (r=0.2986, p=0.051), intended to represent an oxidation potential inhibited by neutralization potential. All these correlations became insignificant (p=0.073 to 0.397) when the five sites having NETNP higher than 80 tons/1000 tons were excluded from the analysis. Including the acid and alkaline end-members of the set of all possible overburden compositions is expected to yield a higher correlation coefficient because overburden columns totally dominated by acid or alkaline strata produce analogous drainage quality. However, these correlations fail in the crucial hard-to-predict cases.

The significance of the correlations shown in Table 4 did not change markedly when AP and NETNP values were calculated using pyritic sulfur rather than total sulfur values. For example, the correlation coefficient for water alkalinity and thickness-weighted NETNP only increased from 0.2225 to 0.2262 when pyritic sulfur values were used. This finding results from the fact that pyritic sulfur and total sulfur contents in these samples were highly correlated. If we had only considered those cases where organic sulfur content was high and represented a variable fraction of total sulfur, AP and NETNP values based on pyritic sulfur rather than total sulfur would be expected to yield significantly stronger correlations.

Sulfate production in the reclaimed spoil may be affected by inherent differences in pyrite reactivity (Hammack 1988), availability of oxygen (Lusardi and Erickson), juxtapositioning of different rock units in the backfill and other factors. Splits of the samples from this study have been analyzed for thermal pyrite reactivity by evolved gas analysis and the data will be used to determine if an effective pyrite content (some combination of sulfur content and reactivity variables) can better predict drainage quality.

A scatterplot of drainage alkalinity versus volume-weighted NETNP (fig. 3) illustrated the lack of predictive value in this overburden variable alone. However, boundaries can be drawn to delineate the acid or alkaline character of the drainage. At NETNP values greater than 80 tons/1000 tons, all sites produced alkaline drainage. No such clear boundary was found on the acid end of the spectrum, probably because the data set did not include equally acid-dominated sites. Such sites usually fail to gain permit approval.

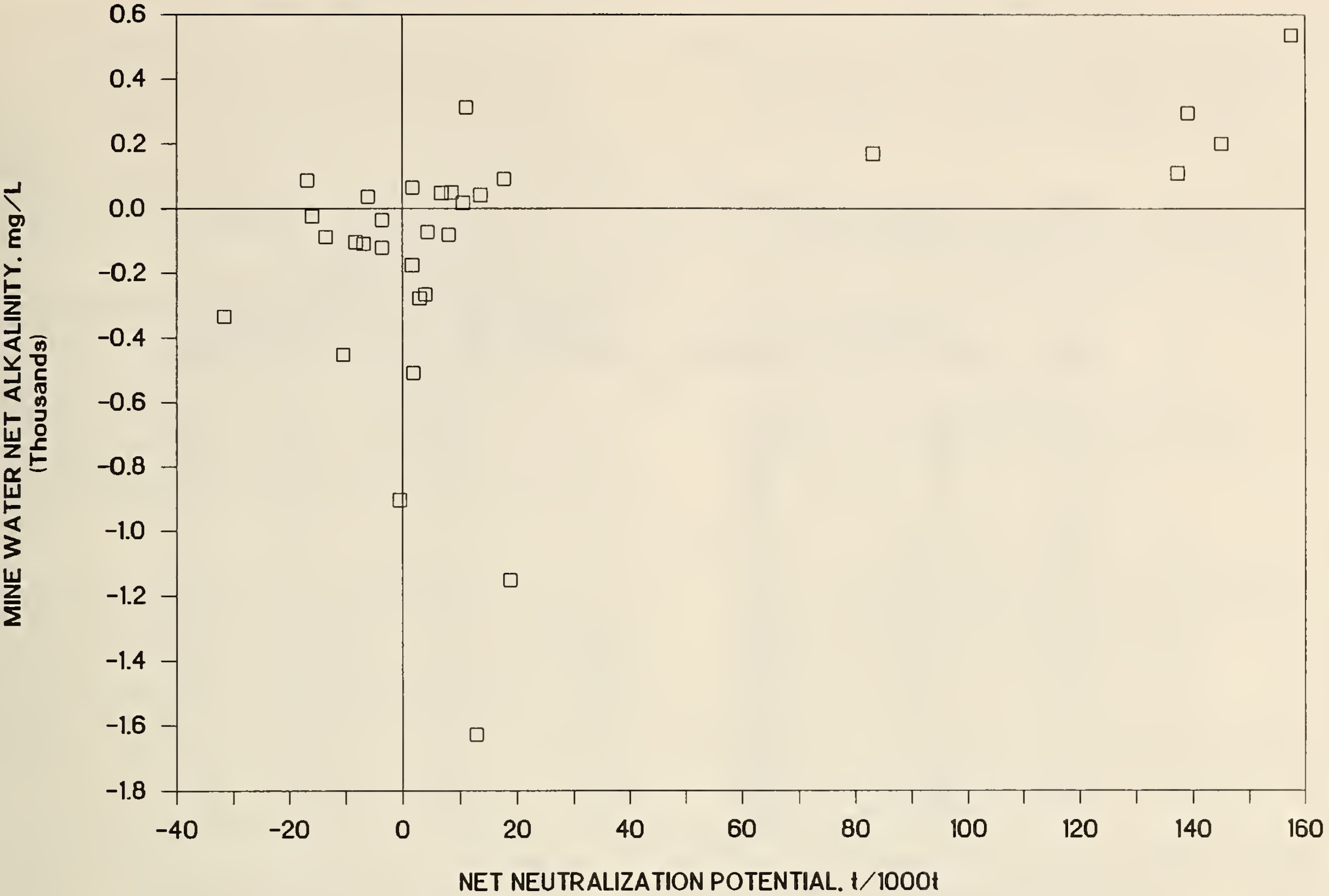

Figure 3.—Scatterplot of volume-weighted net alkalinity versus volume-weighted NETNP for all sites.

Intermediate boundaries are arbitrary:

0<NETNP<20:	acidic drainage in 8 of 15 sites
NETNP<10:	acidic drainage in 15 of 20 sites
NETNP< 0:	acidic drainage in 9 of 11 sites

Clearly, sites having volume weighted NETNP values lower than 20 tons/1000 tons were dominantly acid producers.

Simulated Weathering

The simulated weathering procedure was applied to all overburden samples from 18 of the study sites. Results of weathering tests, along with acid-base account results for the same sites are shown in Table 5.

Correlations were calculated that related weathering test parameters to actual drainage parameters (Table 6). The only significant relationship was between weathering sulfate and drainage sulfate (r=0.4059, p=0.046). These correlations suggest that the laboratory procedure somewhat simulated sulfate production as intended but failed to simulate subsequent neutralization processed that increase alkalinity and precipitate iron. As with the acid-base account, the direct correlation was not strong enough to predict post-mining drainage quality.

Failure to mimic the neutralization processes, and thereby predict drainage alkalinity and iron concentrations, could result from the laboratory tests being conducted on individual strata at atmospheric pCO_2 levels. Both elevated CO_2 and sequential positioning of alkaline and acidic strata affect the amount of carbonate minerals dissolved. No leachate sample exceeded 100 mg/L net alkalinity, while many post-mining drainage samples had net alkalinity in the range of 100 to 620 mg/L.

Samples from five of the study sites were also weathered in the laboratory as thickness-weighted composites of all overburden strata. Leachates from these combined samples sometimes exceeded 100 mg/L net alkalinity. While conclusions drawn from such a small data set are tenuous, this result suggests the intriguing possibility that neutralization reactions that occur in the field can be simulated in the laboratory if the neutralizing strata are exposed to leachate from acidic strata.

Table 5.--Summary of data for sites analyzed by the simulated weathering test[1]

Site ID	Post-mining Water Quality flow-weighted, mg/L		Pre-mining Data			
			Simulated weathering volume-weighted cumulative load, mg		Acid-base account volume-weighted tons/1000 tons	
	Alkalinity	Sulfate	Alkalinity	Sulfate	AP	NETNP
32	-1150.	4020.	-40.2	239.	5.54	18.8
14	-903.	1010.	7.66	48.3	7.31	-0.49
29	-509.	1430.	-41.6	106.	11.6	1.92
18	-453.	695.	-210.	208.	19.2	-10.4
12	-278.	1940.	2.08	37.5	2.35	2.99
19	-176.	819.	24.0	67.7	1.57	1.73
8	-109.	737.	-17.9	146.	13.0	-6.75
28	-81.3	741.	-4.69	57.5	6.75	8.18
4	-72.6	832.	17.6	54.8	15.0	4.38
21	-36.8	761.	26.5	108.	14.8	-3.54
31	64.8	258.	24.8	83.7	18.3	1.86
11	87.4	332.	-174.	281.	32.5	-16.8
6	91.7	797.	39.5	72.2	13.5	17.8
13[2]	109.	259.	22.7	27.1	1.47	7.25
5	170.	1040.	17.7	92.7	22.0	83.2
22	201.	2280.	-280.	995.	51.8	145.
25	313.	695.	20.7	199.	29.9	11.2
23	536.	3310.	41.6	315.	25.8	157.

[1] All values rounded to 3 significant figures or a maximum of 2 decimal places.
[2] Site 13 is thickness-weighted rather than volume-weighted.

Table 6.--Correlations between flow-weighted water quality parameters and simulated weathering test parameters.

Overburden variables, cumulative load, mg	Correlation coefficient (probability) Water variables, flow-weighted mg/L		
	Net alkalinity	Sulfate	Iron
Straight average			
Net alkalinity.....	-0.0436 (0.432)	0.1633 (0.259)	0.0193 (0.470)
Sulfate...........	0.2554 (0.153)	0.2308 (0.178)	-0.1680 (0.253)
Volume-weighted			
Net alkalinity.....	0.0880 (0.364)	-0.0861 (0.367)	-0.1033 (0.342)
Sulfate...........	0.2234 (0.186)	0.4089 (0.046)	-0.2276 (0.182)

CONCLUSIONS

The results of this study confirmed that the overburden analysis methods tested do not adequately predict post-mining drainage quality when used alone. This result is not surprising, as overburden analytical data is only one component of the pre-mining site assessment. Mine operators and regulatory authorities utilize other data and past experience in judging the environmental suitability of a proposed mine.

Examination of water quality data alone showed a high degree of temporal and lateral variability in contamination levels at a single site. Further, the data showed that pyrite oxidation was accompanied by varying degrees of neutralization. While these findings are consistent with the literature and fully expected, they serve to remind us that prediction of overall water quality from the whole mine system and prediction of individual seep water quality are two different things.

Results obtained from the acid-base account confirmed that the use of a 5 ton/1000 ton deficiency of neutralizers (NETNP < - 5 tons/1000 tons) to delineate acid-producing strata is invalid as a predictive tool. Each of the sites used in this study contained at least one lithologic unit that was potentially acid-producing by this standard. Yet only about half the sites produced acidic drainage.

Qualitative boundaries were found for the acid-base account to delineate the alkaline or acidic character of the overburden. All sites having a volume-weighted NETNP greater than 80 tons/1000 tons yielded alkaline drainage. In contrast, the majority of sites having a volume-weighted NETNP less than 20 tons/1000 tons yielded acid drainage. Unfortunately, no sites were found having NETNP in the range of 20 to 80 tons/1000 tons; this range is left as a gray area in predicting acidic or alkaline drainage. Additional data, already available in mining company and regulatory agency files, should be used to test and further refine these boundaries.

The weathering procedure used in this study failed to yield an accurate prediction of water quality and failed to delineate boundaries for drainage of differing acid/alkaline character. The correlation between sulfate produced during simulated weathering and sulfate concentrations observed in the field suggested that pyrite oxidation can be mimicked in the laboratory. Alkalinity-generating processes were not mimicked by this method. Limited data from laboratory weathering showed at least a potential for better simulation of neutralization processes when the overburden strata were composited into a single sample prior to weathering.

It is important to pursue improved means of predicting post-mining drainage quality because of the environmental and economic repercussions of incorrect predictions.

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RELATIONSHIPS BETWEEN THE INITIAL GEOCHEMISTRY AND LEACHATE CHEMISTRY OF WEATHERING OVERBURDEN SAMPLES

Robert S. Hedin and Patricia M. Erickson[2]

Abstract.--The relationships between geochemical measurements and the chemistry of leachates collected in weathering tests were explored for 139 overburden samples. All samples were analyzed for total sulfur (ST) and neutralization potential (NP) and 95 had sulfur fractionated into pyritic, sulfate, and organic forms. All samples were weathered for 6-8 weeks in a laboratory, and leachates were collected and analyzed weekly for acidity, alkalinity, and sulfate. All data were normalized with logarithmic transformations.

Cumulative sulfate produced in the weathering tests was strongly correlated with total sulfur (r=+.83). The relationship with pyritic sulfur was much weaker. NP had a negative influence on sulfate production, but the correlation was weak (r=-.27), especially for samples with NP less than 30 tons per 1000 tons. Multiple regression analyses relating weekly sulfate production to neutralization potential and sulfur forms identified sulfate sulfur as the most important independent variable. Pyritic sulfur was not a significant factor in any week's analysis. When only samples that had produced more sulfate than could be accounted for by sulfate sulfur measurements were considered, pyritic sulfur became a significant component in the sixth week, and the dominant component in the eight week.

Cumulative acidity/alkalinity, expressed on a single scale, was significantly correlated with total sulfur (r=+.37), NP (r=-.43) and the difference of neutralization and acid potential Net NP (r=.61). Estimates were made of the cumulative neutralization generated by each weathered sample by comparing sulfate and acidity/alkalinity production. For most samples, less than 10% of the NP had been consumed in the 6-8 week tests. All samples with more than 25% consumption produced acidic leachates.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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INTRODUCTION

Two procedures commonly used in acid mine drainage prediction efforts are acid-base accounting and weathering tests. Both procedures require that the overburden be adequately sampled. With acid-base accounting, the samples are analyzed for neutralization potential and sulfur content, which is converted into an acid potential. These values are compared to determine whether the sample is likely to develop acidic or alkaline conditions. Samples are often aggregated, by various weighting methods, so that the acidity or alkalinity of the entire overburden can be represented by a single value.

The acid-base method has several important limitations. Sulfur measurements, using current procedures, cannot account for the variability that exists in sulfide reactivity (Caruccio 1969; Hammack 1985; Hammack, elsewhere in these procedings). The method used to determine neutralization potential can give inflated results if the sample contains significant amounts of siderite (Caruccio 1967). More importantly, acidity and alkalinity are generated by quite different processes that are not additive. Caruccio and Parizek (1967) have suggested that a better approach is to artificially weather samples and monitor the chemistry of regularly collected leachates. After an appropriate period, samples are characterized by their actual production of acidity or alkalinity.

The acid-base method is preferred by most mine operators because it has significant cost advantage over weathering tests. When overburdens are dominated by either acidic or basic materials, errors introduced by the acid-base procedure are not important. However, when overburdens are roughly balanced with respect to acidic and basic materials, the errors of the accounting method may be unacceptable and weathering tests may be required. Despite these additional efforts, post-mining water quality is often quite different from its predicted composition.

We evaluated the usefulness of these methods for sites with balanced overburden chemistries by comparing the results of acid/base accounting and weathering tests to measured post-mining water quality. In another paper we describe the relationships between these prediction methods and the drainage chemistry (Erickson and Hedin, elsewhere in these proceedings 1988). In this paper we discuss the relationship between the methods. We try to fit these relationships within the current tenets of spoil acidification, and where they do not mesh, we identify theoretical or methodological problems that cause the failures.

METHODS

The overburdens at 32 active mining sites were described and sampled. At 9 sites preserved overburden cores were inspected and sampled. At 23 sites fresh highwalls were described and channel samples were collected after removing weathered surface materials. Each overburden was described by the thickness and type of individual stratigraphic unit. The entire length of each unit was sampled and, when this resulted in an unmanageable amount of material, a subsample was taken. All samples were stored in sealed plastic bags.

A total of 264 samples were collected, and a determination of total sulfur (ST) (Fisher automated sulfur analyzer) and neutralization potential (NP) was made for each (Sobek et al. 1974). (See (table 1) for acronyms of all variables discussed). For samples with a total sulfur content greater than 0.5% (n=95), sulfur was fractionated into organic (SO) sulfate (SS) and pyritic (SP) forms using leaching procedures described by Sobek et al. (1974). We use the term "pyritic" to refer to the sulfur which can be extracted by HNO_3 but not by HCl. This value is believed to represent all forms of reduced sulfur, that upon oxidation, would produce acid products.

Neutralization potentials were expressed in tons of $CaCO_3$ equivalent per 1000 tons.[3] Sulfur contents were expressed as percent of dry weight. Acid potentials (AP), expressed in the same units as neutralization potential, were estimated by multiplying the total sulfur content by 31.25. Net NP was calculated by subtracting acid potential from neutralization potential.

Student's t-test comparisons of the pyritic sulfur ($t=0.83$, $P>0.05$) and sulfate sulfur ($t=1.30$, $P>0.05$) contents of samples collected from highwalls and from preserved cores revealed no significant differences. Thus, differential weathering of highwall and preserved core samples was not indicated and all samples were subsequently pooled.

Weathering tests were performed on all 152 samples from 16 mines. Sample splits of 300 grams were crushed to pass a 2mm sieve, and placed in plastic boxes which were continuously aerated with humid air for 6-8 weeks. Each sample was initially spiked with 10 ml of acid mine drainage to insure the presence of iron-oxidizing bacteria. At weekly intervals the boxes were filled with 300 ml of distilled water and drained after one hour. The volume of the collected leachate was determined, and the samples were analyzed for pH, sulfate, acidity, alkalinity, and iron.

Weathering test results were expressed as milligrams of sulfate or acidity, which were calculated by multiplying measured concentrations by the volume of leachate collected (table 1). Unless otherwise noted, the results of the first leachate were not included in calculations.

Unit sulfate production, (USP), which related the cumulative milligrams of sulfate leached to the grams of total sulfur present in the sample, was calculated:

$$USP = SO_4\ mg/(sample\ grams * ST)$$

An estimate of the total neutralization generated, (NG), was calculated from the stoichiometry of pyritic oxidation in the absence of secondary neutralization as two moles of H^+ associated with each mole of sulfate:

$$NG = (SO_4\ mg * 100/96) - acidity$$

where acidity was expressed as a positive value, and alkalinity was a negative value.

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[3] The unit derives from agronomic applications, where 1000 tons is equivalent to an acre-plow layer. Parts per thousand (PPT) is the generic term.

Table 1.--Key to Abbreviations and Calculations.

Abb.	Variable	unit	Measurement or Calculation
GEOCHEMICAL MEASUREMENTS			
ST	Total Sulfur	% of dry wght	LECO Sulfur Analyzer[1]
SP	Pyritic Sulfur	% of dry wght	acid leaches and LECO[1]
SS	Sulfate Sulfur	% of dry wght	acid leaches and LECO[1]
SO	Organic Sulfur	% of dry wght	acid leaches and LECO[1]
NP	Neutralization Potential	tons/1000 tons	titration[1]
AP	Acid Potential	tons/1000 tons	ST X 31.25
NETNP	Net NP Potential	tons/1000 tons	NP - AP
NP/AP	Ratio	ratio	NP / AP
LEACHATE MEASUREMENTS			
SO4	Cummulative Sulfate Production	milligrams	sum of (sulfate mg/L X L leached)
ACID	Cummulative Acidity Production	mg $CaCO_3$ equiv	sum of ((acidity-alkalinity) mg/L X L leached)
NG	Neutralization Generated	mg $CaCO_3$ equiv	(SO4 X 100/96) - ACID
NC	Neutralization Consumed	% of NP	NG / NP
USP	Unit Sulfate Production	Sulfate per gram of total sulfur	SO4 / (ST X 300 gm/sample)

[1] methods from Sobek et al. 1974

Data were analyzed using the SPSSX computer package. We used a 0.05 probability level to judge the significance of correlations and regressions. Alkalinity was treated as negative acidity so that both could be expressed on a single scale. None of the data were normally distributed in their raw form. Normal distributions of ST, SP, SS, NP, USP, NG, and sulfate were obtained with logarithmic transformations. Transformations did not normalize organic sulfur determinations, so statistical evaluations of this minor sulfur fraction should be viewed cautiously. Logarithmic transformations of acidity values were made after adding 150 to each to correct for negative (alkaline) values. For a similar reason, Net NP values were increased by 50 before making logarithmic transformations.

Because we were most concerned with roughly balanced overburdens, we eliminated samples with extreme ST or NP values from the analyses. This restriction caused the elimination of one sample with a total sulfur content of 8.2% and 12 samples with NP > 200. The data set analyzed thus contained 139 samples for which weathering results, neutralization potential and total sulfur were known, and a subset of 51 samples for which sulfur fractions were also known.

RESULTS

The average sample had a total sulfur content of 0.64% and an neutralization potential of 13.3 tons $CaCO_3$ per 1000 tons (n=139). The average difference between neutralization potential and acid potential (Net NP) was -7.10. Sulfur was fractionated for 51 samples which averaged 1.47% total sulfur, of which 77% was classified as pyrite, 17% as sulfate, and 6% as organic sulfur.

The average sample produced in the weathering tests a total of 281 mg of sulfate and 98 mg of net acidity (calculated: acidity minus alkalinity). The 51 samples with fractionated sulfur forms, produced on average 624 mg of sulfate and 291 mg of net acidity.

Cumulative Sulfate Production and Acid Potential

The first hypothesis about relationships between leachate chemistry and sample geochemistry considered was that sulfate production was related to a sample's total sulfur content. This expectation was strongly supported (table 2, figure 1). Regression of acid potential on sulfate indicated the following log-log relationship:

$$\log(\text{sulfate}) = 0.675 \log(\text{AP}) + 1.446 \quad (r^2 = .77,\ n=139)$$

This estimate of acid potential was based on total sulfur values. We expected that acid potential values based on pyritic measurements (APSP) would result in a stronger relationship. Instead, regression analysis revealed a similar equation, but a much weaker relationship.

$$\log(\text{sulfate}) = 0.754 \log(\text{APSP}) + 1.510, \quad (r^2 = .35,\ n=51)$$

The strongest correlation between sulfate production and a sulfur fraction was with sulfate sulfur (r=.78). Multiple regression of sulfur fraction percentages (SP, SO, SS) and NP on cumulative sulfate production, produced the

Table 2.--Pearson correlations between sample geochemistry and leachate chemistry.

Geochemical Measurement	Leachate measurement Sulfate	Acidity	USP	NG
AP	$+.83^{***}$	$+.37^{***}$	$-.46^{***}$	$+.84^{***}$
NP	ns	$-.43^{***}$	$-.27^{**}$	$+.33^{***}$
Net NP	$-.55^{***}$	$-.61^{***}$	ns	$-.30^{***}$

** $P<0.01$; *** $P<0.001$; ns $P>0.05$
All variables were log-transformed before calculations.

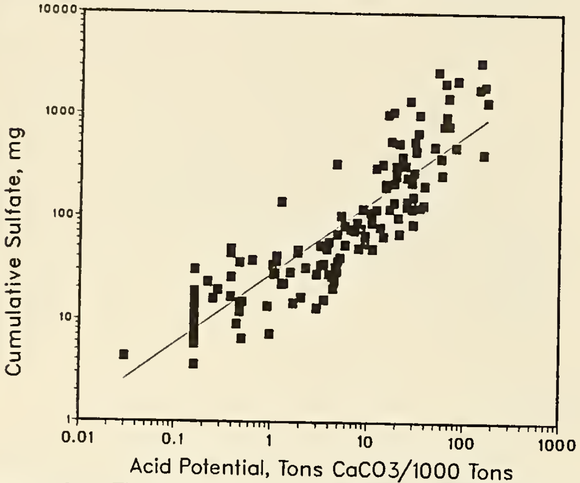

Figure 1.--The relationship between cummulative sulfate production by weathering samples and their intitial acid potential. Coefficients of the regression line are given in the text.

following relationship.

$$\log(\text{sulfate}) = 0.631 \log(\text{SS}) + 0.189 \log(\text{SO}) + 3.434,\ (r^2 = .68,\ n=51)$$

Pyritic sulfur and neutralization potential were not significant components of the regression equation.

Cumulative Sulfate Production and Neutralization Potential

Several studies have produced results that suggest that neutralization potential has a negative influence on sulfate production, presumably because it inhibits activity by iron oxidizing bacteria (Caruccio, et al. 1980; Williams et al. 1982, Poissant and Caruccio 1986). We tested this hypothesis by comparing NP to cumulative sulfate production and unit sulfate production.

NP was not significantly correlated with cumulative sulfate production (table 2). This finding was further supported by the observation that several limestone samples (excluded from these analyses) produced very high amounts of sulfate. At the sites where these limestones were collected, the drainage was characterized by alkaline water with extremely high sulfate concentrations. Clearly, high NP does not, by itself, cause radical reductions in sulfate production.

Caruccio and his students have tested for a neutralization effect by comparing unit sulfate production (USP) to alkaline production potentials. Samples with high NP relative to sulfur, generally result in lower production of sulfate per unit of sulfur. Caruccio has only discussed a small number of samples, all with total sulfur contents > 1% (Caruccio, Geidel and Pelletier 1980). We tested a larger number of samples with a wider range of sulfur values. Because very low sulfur values inflate USP values and the variation in very low sulfur values may be instrument or operator related, only materials with ST contents greater than 0.05% were considered in our analysis. A significant, negative correlation was found between NP and USP, but it was weak (table 2, figure 2).

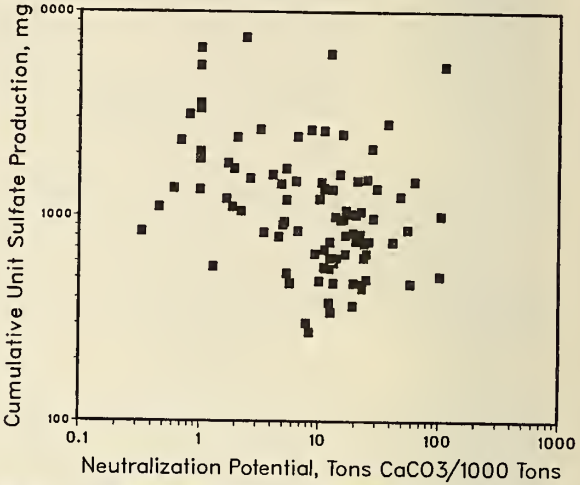

Figure 2.--The relationship between unit sulfate production and nuetralization potential.

Cumulative Sulfate Production, AP and NP

Because both acid potential and neutralization potential influence sulfate production, a multivariate analysis was used to test the complexity of the relationship. Various combinations of AP and NP have been suggested as appropriate for acid mine drainage prediction models. We tested NP, AP, Net NP, and the ratio of NP to APST (NP/AP). The best fit was with AP and the ratio.

$$\log(\text{sulfate}) = 0.484 \log(\text{AP}) - 0.215 \log(\text{NP/AP}) + 1.608,\ (r^2 = .80,\ n=139)$$

Note that when NP is less than AP, the ratio is less than one and log(NP/AP) is a negative value. This results in a higher prediction of sulfate production. At ratios greater than 1.0, the sulfate production prediction is decreased. This relationship indicates that NP only inhibits sulfate production when it is present in excess.

Weekly Sulfate Production by Weathering Samples

Thus far, only cumulative production of sulfate during the weathering tests has been discussed. Because leachates were collected and analyzed on a weekly basis, analysis of temporal changes in the relationships was possible. For each week's data, regression equations were calculated which related that week's sulfate production to the original measurements of neutralization potential, pyritic, sulfate and organic sulfur. Of the 51 samples analyzed, all were weathered for at least 6 weeks, and 45 were weathered for 8 weeks.

We predicted that the first week's sulfate production would be strongly related to sulfate sulfur because during this first leach much of the rock's original sulfate content would be dissolved. In subsequent weeks we expected that pyritic sulfur would be the most important component, because of oxidation, and that NP would have a minor negative effect on sulfate production.

Our first prediction was supported by the regression analysis (table 3). Sulfate sulfur was the most important geochemical component and pyritic sulfur was not a significant factor. Unexpectedly, sulfate sulfur remained a significant part of the regression equations for the entire weathering period (8 weeks). Pyritic sulfur never became a significant component. Neutralization potential acted as a negative factor after four weeks. Organic sulfur was a significant factor throughout the experiment, but its low degree of contribution and its non-normal distribution makes specific interpretations difficult.

Table 3.--Relationships between sample geochemistry and weekly sulfate production. The coefficients values were calculated for the equation:
$SO4 = b_1(SP) + b_2(SS) + b_3(SO) + b_4(NP)$

Week	r	b_1	b_2	b_3	b_4
1	.69	ns	0.70	0.32	ns
2	.77	ns	0.72	0.27	ns
3	.84	ns	0.71	0.14	ns
4	.82	ns	0.66	0.21	ns
5	.86	ns	0.64	0.24	-0.17
6	.87	ns	0.72	0.18	-0.25
7	.82	ns	0.59	0.24	-0.24
8	.75	ns	0.56	0.22	-0.25

ns $P>0.05$; all other coefficients, $P<0.05$;
All variables were log-transformed before regression analysis.

To further explore these unexpected findings, samples were classified each week according to the fraction of sulfate sulfur leached. This fraction was calculated by dividing the cumulative sulfate leached by the amount of sulfate available in the original sample. Samples with a fraction greater than 1.0 had produced more sulfate than could be accounted for by the original sulfate sulfur content. We tested the hypothesis that sulfate production by samples which had been, theoretically, depleted of their original sulfate sulfur content, was more dependent on pyrite than samples for which residual sulfate sulfur still existed.

The highest r-square values for the regression equation relating sulfate production to SP, SS, SO and NO were obtained when a ratio of 0.80, not 1.00, was used as the sorting criteria. We suspect that this may be because some of the sulfate sulfur present was not readily leached by our weathering procedures. The correlations and r-square values obtained were consistently higher than those obtained in the initial analysis.

Table 4.--Relationships between sample geochemistry and weekly sulfate production that are sorted according to the proportion of sulfate leached to that originally available.

a.--Samples with CUMSO4/SSAVAIL > 0.80
$SO4 = b_1(SP) + b_2(SS) + b_3(SO) + b_4(NP)$

Week	n	r	b_1	b_2	b_3	b_4
1-3	0					
4	14	.84	ns	0.76	ns	ns
5	22	.90	ns	0.67	0.22	-0.18
6	26	.91	0.52	0.64	ns	-0.36
7	25	.89	0.46	0.44	0.15	-0.33
8	30	.84	0.84	0.36	ns	-0.40

b.--Samples with CUMSO4/SSAVAIL $\leq$ 0.80
$SO4 = b_1(SP) + b_2(SS) + b_3(SO) + b_4(NP)$

Week	n	r	b_1	b_2	b_3	b_4
4	37	.87	ns	0.87	ns	ns
5	29	.91	ns	0.86	0.13	ns
6	25	.94	ns	0.98	ns	-0.16
7	20	.92	ns	0.93	ns	ns
8	15	.79	ns	0.85	ns	ns

ns $P>0.05$; all other coefficients, $P<0.05$
CUMSO4 is the cummulative sulfate produced by samples in the appropriate week; SSAVAIL is an estimate of the total amount of sulfate contained by each sample before weathering;
All variables were log-transformed before regression analysis.

Sulfate production by samples with less than 80% of the original sulfate leached was very strongly related to sulfate sulfur and generally unrelated to neutralization potential, pyritic or organic sulfur (table 4b). The importance of sulfate sulfur did not decrease between the fourth and eighth weeks for these samples.

The equations for samples with more than 80% of the original sulfate accounted for in the leachate, were considerably different (table 4a). Pyritic sulfur was a significant factor after 5 weeks and the most important factor at eight weeks. Sulfate sulfur was a significant component of all equations, but its importance decreased with each additional week. Neutralization potential was a significant negative influence in all but the fourth week.

Two alternative explanations can account for the unexpected importance of sulfate sulfur and the relative unimportance of pyritic sulfur in predicting sulfate production. One explanation is that the sulfate sulfur may not have been completely solubilized during the first leaching. Instead, it could have been gradually released over the 6-8 weeks of testing. We find little theoretical support for this hypothesis because equilibrium and kinetic factors favor complete sulfate dissolution. Common sulfate minerals, such as gypsum and jarosite, have very rapid dissolution kinetics and have high solubilities. All of the leachates, which sat for 60 minutes before being drained off, were undersaturated with respect to these minerals. More importantly, this explanation cannot explain the negative influence of neutralization potential since it is unlikely that calcite or dolomite effect the solubility of sulfate minerals or the kinetics of their dissolution. It is possible that sulfate is contained within particles that are not penetrated by the solvent (distilled water) until they undergo weathering. We find this process also difficult to support.

Our second explanation is that the sulfate sulfur measurement technique is flawed. In our method, determinations were made of total sulfur for a raw sample and for one which was leached with HCl to remove all sulfate sulfur. Sulfate sulfur was calculated as the difference of the two measurements. A crucial assumption of this method is that HCl does not effect reduced forms of sulfur. Although valid for crystallized, stable forms of pyrite, the assumption is not true for unstable mono-sulfides. Soil scientists who work with sulfide-containing sediments commonly use HCl to dissolve and quantify reduced sulfur. When we perform HCl leaches on overburden samples, we commonly observe hydrogen sulfide fumes, an indication of sulfide oxidation (R. Hammack, personal communication). This fraction of reduced sulfur is the most unstable and most easily oxidized. In a weathering experiment, we would expect that these sulfur compounds would be the first to oxidize and, if present in sufficient quantities, significantly effect sulfate production during the first several weeks of weathering. We would also expect that neutralization potential, if present in sufficient quantities, could inhibit this source of sulfate. Thus, the finding that NP has a significant negative role before pyrite has a significant positive one is not unexpected.

Cumulative Net Acidity and AP and NP

Net acidity (acidity minus alkalinity) produced in leaching tests was significantly correlated with both acid potential and neutralization potentials, but was most strongly related to the net NP (table 2). A plot of net NP against net acidity is shown in figure 3. Samples with large excesses of neutralization potential never produced cumulative alkalinities (negative net acidities) greater than 100 mg $CaCO_3$ equivalent, while several samples with large excesses of acid producing potential resulted in more than 1000 mg of cumulative net acidity. This result is primarily an artifact of the weathering experiment and would be expected for all tests with a similar design. Constant aeration of the weathering boxes prevented the accumulation of carbon dioxide and thus limited alkalinities to approximately 100 mg over the 6-8 weeks of weathering. Even limestones, which are not included in Figure 3, never produced more than 200 mg of alkalinity (40-50 mg/L). These conditions do not represent those commonly observed in spoil piles (Lusardi and Erickson, 1985).

All samples, but one, with positive Net NP produced alkaline or only slightly acid leachates (less than 50 mg $CaCO_3$ equivalent of acidity). This relationship held until Net NP reached -8.0 tons/1000 tons. Below this value there was considerable variation in the relationship between Net NP and net leachate acidity. In particular, several samples that were extremely deficient in neutralization potential (negative Net NP) produced alkaline leachates. For two of these samples sulfate levels were high, suggesting that the high alkalinity was due to a high amount of neutralization. For the other samples with unexpectedly high alkalinities, sulfate production was low, suggesting limited acid production despite high acid producing potentials.

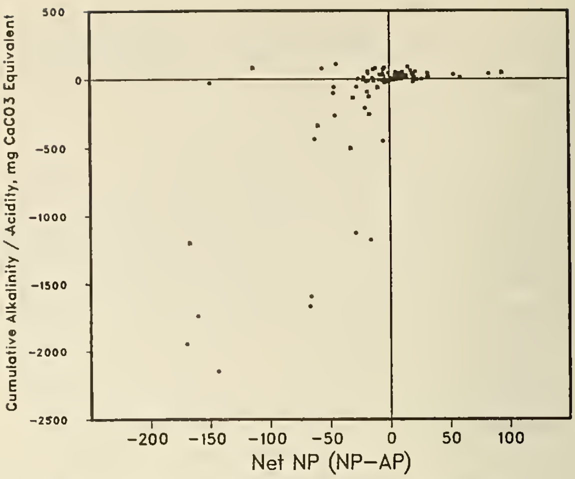

Figure 3.--The relationship between cummulative production of net acidity by weathering samples and their initial Net NP.

The best fit regression relating net acidity to geochemical measurements was:

$$\log(\text{Acidity}) = -0.364 \log(\text{NP/AP}) - 0.257 \log(\text{AP}) - 0.802 \log(\text{Net NP}) + 4.150$$
$$(r^2 = .54,\ n=139)$$

As with sulfate production, a logarithmic model best explained production of net acidity, but the explained variation was less. This is partially a result of the difficulty in fitting a single model to data that is influenced by two different processes. Generation of alkalinity is limited by solubility constraints forced by the gas compositions in the weathering vessels. Acidity is only limited by the rate of acid potential and, for our purposes, is unconstrained by any solubility limitations.

In a second analysis, the influence of alkalinity limitations was minimized by only considering samples with Net NP less than -8.0. The relationship improved considerably and the best equation was non-exponential:

$$\log(\text{Acidity}) = 0.004\ \text{AP} - 0.036\ \text{NP} - 0.828\ \text{NP/AP} + 2.550,\ (r^2 = .77)$$

Again, the ratio of neutralization potential to acid potential, not the difference, is a significant addition to the model.

Cumulative Neutralization Generation

Cumulative generation of neutralization was estimated from cumulative sulfate production and cumulative acidity/alkalinity. The calculation is based on the assumption that two moles of H^+ are associated with each mole of sulfate. When the measured acidity of a leachate sample is less than the acidity estimated from sulfate measurements, then a calculable amount of neutralization has occurred. Generation of neutralization (NG) was significantly related with all measures of acid potential and neutralization potential (table 1). Multiple regression revealed that a logarithmic relationship with APST and NP gave the best relationship.

$$\log(NG) = 0.551 \log(AP) + 0.138 \log(NP) + 1.428 \quad (r^2 = .72)$$

Because high NG is only possible when a high amount of sulfate production has occurred, acid potential is more important than neutralization potential. Unlike the acidity calculations, separating the data into acidic and alkaline overburden samples did not improve the relationship. This was because NG was less constrained by solubility limitations than raw alkalinity measurements. Many alkaline samples had high sulfate values, which resulted in high NG estimates.

The above equation also suggests that NP was rarely a limiting component of the generation of neutralization. To determine the percentage of neutralization consumed in the weathering experiments, we compared the neutralization generated to the neutralization potential originally measured.

$$\text{Neutralization Consumed} = \text{NG mg} / \text{NP mg}$$

Less than 10% of NP had been consumed in 58% of the samples. Four of 136 samples had consumption percentages greater than 100 indicating that the neutralization potential had been theoretically exhausted. These samples produced some of the most acid leachates. All samples with more than 25% consumption produced acidity (figure 4). All of these samples had NP values less than 5.0. Samples with similar NP values, but lower estimates of consumption, generally had alkaline or only slightly acid leachates.

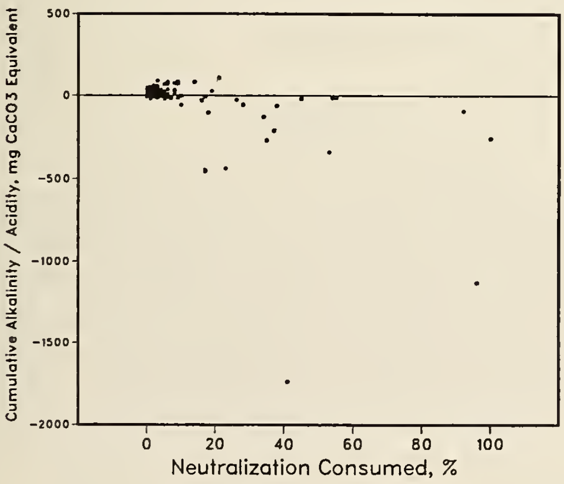

Figure 4.--The relationship between cummulative production of net acidity by weathering samples and the percentage of NP consumed during the weathering tests.

DISCUSSION

These results support the general tenets of the spoil acidification process. Sulfate production by a weathering sample is strongly correlated with its sulfur content. The relationship is best characterized by logarithmic equations. Neutralization potential has an inhibitory influence on sulfate production, but the effect is variable. It cannot be determined from these results whether NP actually inhibits sulfate production, or if it is negatively correlated with sulfur reactivity. The acidity of a sample is strongly related to both its acid producing potential (based on total sulfur) and its neutralization potential. Both models of sulfate and acidity production are improved by the incorporation of the ratio of neutralization to acid potentials.

We also found some unexpected results. Pyritic sulfur was not a better predictor of a leachate's sulfate content or its net acidity than total sulfur. This result may be an artifact of the limited length of our weathering tests (6-8 weeks) since, for some samples, pyrite was increasing in significance in the final weeks of weathering. However, this explanation indicates that the results of weathering tests are strongly dependent on the period over which they are conducted. Because the goal of these tests is to obtain an estimate of the acid potential, it is important that they are conducted until significant pyritic oxidation and acid production has occurred. According to Caruccio et al. (1980), the tests should be conducted until the rate of sulfate production levels off which generally takes 5-10 weeks. Our results, which are based on obtaining a statistically significant relationship between sulfate production and the pyritic content of the sample, suggest even eight weeks is not sufficient. During this study we reviewed an alarming number of overburden analyses, done by coal companies or consulting firms, which reported leachate results after only 3-4 weeks.

The expected relationship between sulfate production and pyritic sulfur only existed for samples which were, theoretically, completely leached of their original sulfate content and had been weathering for at least six weeks. It might thus be appropriate to determine the length of a weathering test by the ratio of sulfate leached to sulfate contained in the original sample. Sulfate production rates would not be estimated until more sulfate had been leached than had been measured in the original sulfate sulfur determinations.

The unexpectedly strong relationship between sulfate production and a sample's sulfate sulfur content suggests that sulfate sulfur measurements are in error. It is likely that unstable sulfides are dissolved in HCl during the sulfate sulfur procedure. Although these compounds may be a small fraction of the total pool of reduced sulfur, they represent the most reactive forms and would oxidize very quickly in weathering tests. If quantifiable, this methodological error might be developed into a useful indicator of the reactivity of pyritic sample. We are currently exploring this possibility by analyzing the relationship between sulfate sulfur estimates and evolved gas analyses.

Finally, we address the problem of predicting drainage chemistry on a mine level. Are the errors calculated and discussed in this paper responsible for predictive failures? We think not. The error of our relationships is about 25%, which is not great enough to account for the large differences between expected and actual drainage chemistry observed in our study (see Erickson and Hedin in these proceedings). Indeed, we appear to have an accurate understanding of the acid and sulfate production process under controlled, laboratory conditions. More likely, the failure of the methods lies in conservative assumptions and design features that are inappropriate. In the acid-base accounting method, the assumption is made that all sulfur will oxidize, and all basic materials will dissolve. Several surveys of the sulfur content of abandoned spoil piles have shown that unweathered portions of the spoils retain significant quantities of pyritic sulfur (Lusardi and Erickson 1985; von Demfange and Warner 1975). In our weathering tests, we produced conditions that maximized pyritic oxidation and minimized alkalinity. Both of these problems can be justified when one wishes to make conservative judgments. However, if accurate predictions are the goal, the assumptions and methodologies must be thoroughly reevaluated.

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APPLICATION OF ACID-BASE ANALYSIS TO WASTES FROM BASE METAL AND PRECIOUS METAL MINES[1]

Stuart D. Miller and Gavin S. Murray[2]

Abstract--Acid-base analysis is used to assess the potential for waste materials to generate acid when exposed to an oxidized leaching environment. Even though the procedure was initially developed for coal mine overburden and reject, it has become widely accepted as tool in the assessment of waste rock and processing wastes from base metal and precious metal operations.

This paper examines the applications of the acid-base analysis to non-coal situations based on the authors' direct experience at more than 30 base metal and precious metal projects in Australia, New Zealand and Papua New Guinea. The fundamental principles of the technique are outlined and the major potential pitfalls in interpretation and use of acid-base data are described. The paper concludes that the acid-base technique is an essential tool for the assessment of waste characteristics as well as being suitable as a monitoring procedure at non-coal mines. However, the interpretation of results is site-specific and requires detailed geochemical investigation to provide the understanding and data base for this interpretation.

INTRODUCTION

The acid-base analysis has been used extensively for at least 10 years to identify acid forming and potentially acid-forming mining wastes. The procedure reported by Sobek et al. (1978) for coal mining wastes has been applied in many and varied environments, geological materials and in many countries. Even though the procedure was initially developed for coal mine overburden and reject, it has become widely accepted as a tool in the assessment of waste rock and processing wastes from base metal and precious metal operations.

This paper examines the application of the acid-base analysis to non-coal situations based on the authors' direct experience at more than 30 base metal and precious metal projects in Australia, New Zealand and Papua New Guinea. The fundamental principles of the technique are outlined and the major potential pitfalls in interpretation and use of acid-base data are described.

THE ACID-BASE ACCOUNT: THEORY AND PRACTICES

The acid-base account, also known as the Net Acid Producing Potential (NAPP), is calculated from the total sulphur content and the inherent acid neutralizing capacity (ANC) of a material. NAPP is defined as follows:

$$\text{NAPP} = \%\text{S} \times 3.125 - \text{ANC}$$

where ANC and NAPP are in % $CaCO_3$ equivalents.

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A negative NAPP indicates that there is excess neutralizing capacity and that the material is non-acid forming whereas a positive NAPP indicates that the material is acid or potentially acid forming. The pH and electrical conductivity of a saturated paste of crushed (-2mm) material is used to support the NAPP classifications.

Geochemically there are a number of fundamental concerns in the theoretical basis on which the acid-base or NAPP technique is based. The major concerns are as follows:

1. Assumes all sulphur occurs as pyritic sulphide and is acid forming;

2. Assumes all ANC is available to neutralize acid; and

3. Does not consider the kinetics of either the acid forming or acid neutralizing processes.

The first two concerns may be considered to balance each other, however, failure to consider the site specific mechanisms and kinetics when assessing the likely field geochemistry of a particular waste can result in significant error.

The NAPP procedure is an essential tool in waste characterization but the interpretation and identification of the implications for waste management requires a more detailed determination of waste geochemistry. Once the broad principles of the site-specific processes have been identified, a monitoring and management program can normally be developed which is based on the NAPP procedure.

The most important step in carrying out a NAPP assessment of waste rock and ore from a base metal sulphide or gold operation is sample selection. There is generally wide variability in the degree of alteration or mineralization associated with a mineral deposit. Spatial variability in the occurrence of sulphides and carbonates is critical and has been responsible for incorrect predictions of the acid-forming potential of material when composite samples are used in the testing program. It is essential that individual depth samples from a number of drill holes are tested to provide an indication of the variability before composite samples are prepared for any detailed geochemical analysis.

APPLICATION OF ACID-BASE ANALYSIS AT SULPHIDE MINERAL DEPOSITS

General

The objectives of carrying out an acid-base analysis are:

1. Determine the acid-forming characteristics of waste rock, ore and processing wastes;

2. Classify waste rock types with respect to the potential for acid generation;

3. Determine the impact on the quality of drainage from the mine and waste dumps;

4. Provide design and management criteria for waste disposal, pollution control and rehabilitation.

Our experience at more than 30 base metal and precious metal deposits throughout Australia, New Zealand and Papua New Guinea has aimed to provide the engineers with workable and practical design and operational criteria. This includes the classification of waste types, disposal needs and constraints on the operation. With respect to the acid forming characteristics, 4 geochemical types are defined as follows.

	TRIGGER LEVEL CRITERIA		
CLASSIFICATION	pH	%S	NAPP (%CaCO3)
Acid	<4	<0.5	
Acid Forming	<4	>0.5	>0
Potentially Acid Forming	>4		>0
Non-Acid Forming	>4	<0.5	<0

In addition to the above 4 types, a 'barren' classification is frequently applicable for material which is essentially devoid of sulphide and acid neutralizing capacity.

In mineral deposits the mineralogy of sulphides and the content of carbonate have a major controlling impact on the lag period for acid generation and the eventual rate of acid generation. Some materials with less the 2% sulphur can generate acid in less than 6 weeks following exposure, whereas other materials with 30% sulphur may require 20 years of oxidized leaching before acid conditions become established.

Leaching tests are used to provide design and management criteria for controlling acid generation. Column and batch leaching tests are commonly used, and where possible, larger scale field trials are also utilized. Our approach is to use coarse (-25mm) size material in columns and leach under simulated rainfall conditions. This provides an indication of leachate quality, weathering behavior, and incorporates the effect of the kinetics of the acid formation and acid neutralization processes. Batch (humidity cell) leaching tests are generally carried out using dilute sulphuric acid to neutralize any inherent acid neutralizing capacity and create conditions under which acid formation can be examined, including inoculation with a mixed bacteria culture.

The objectives of the leaching test are to provide an indication of the reactivity of sulphides, the presence and likely scale of any lag period for acid generation, the ability of the material to generate acid support bacterially catalyzed oxidation, and the nature of short term leachates.

Case Studies

The variability at any one site can be demonstrated by a plot of sulphur and the acid neutralizing capacity. Figures 1 and 2 show this type of plot for a base metal sulphide deposit in Tasmania, Australia (Figure 1) and a gold deposit in New Zealand (Figure 2).

FIGURE 1: ACID FORMING POTENTIAL - BASE METAL SULPHIDE DEPOSIT

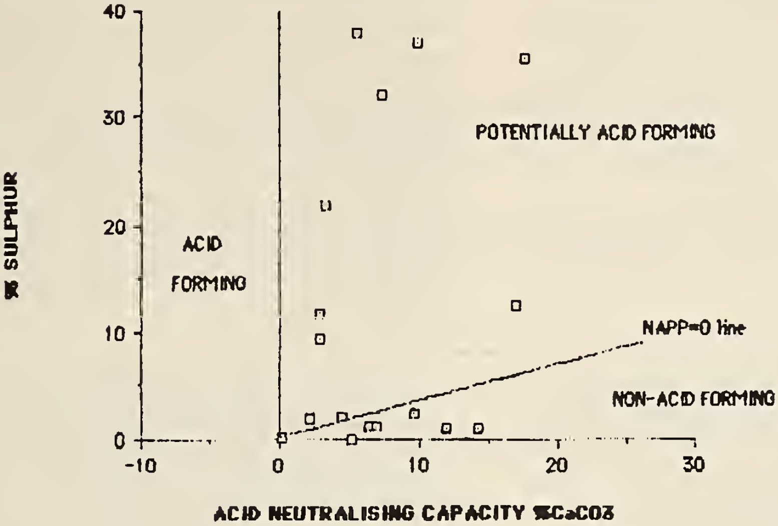
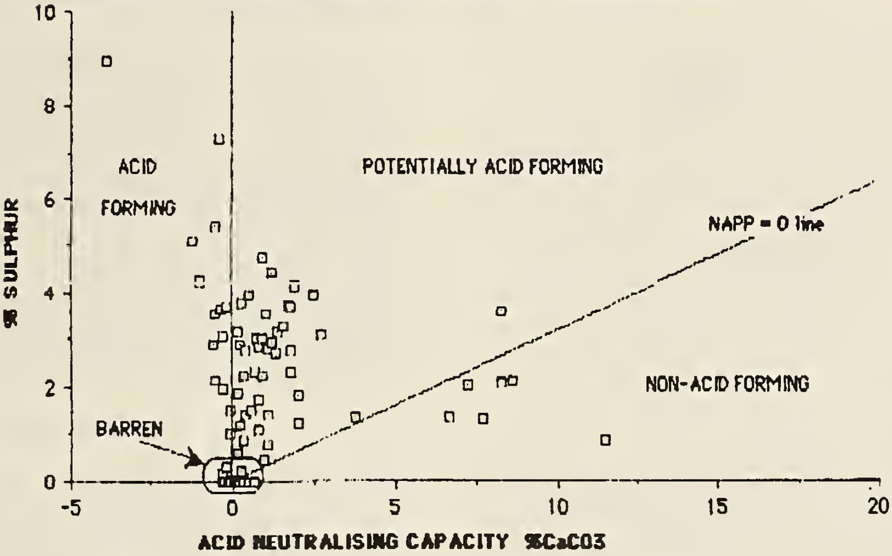


FIGURE 2 ACID FORMING POTENTIAL - GOLD PROJECT



In the base metal sulphide deposit two geochemical waste rock types were identified vis. potentially acid forming and non-acid forming. All samples contain significant levels of carbonate and even the samples with greater than 30% S contain between 5 and 20% CaCO3 equivalent. Leaching studies have been carried out on these rock types which confirms the non-acid nature of the non-acid forming rock but also confirm the very long lag period required for acid generation in the potentially acid forming material. It is predicted that at least 10 years of oxidized leaching will be required before acid is generated in these potentially acid forming rocks. Three years of operational experience supports this prediction. Rock excavated from the underground operation is visually assessed as being acid forming or non-acid forming with occasional check analysis when new areas are opened up. The non-acid material is used for engineering works and the acid-forming material placed in a controlled stockpile area for later use as underground fill in worked out stopes. Mine drainage is currently non-acid with a flow rate of approximately 30 L/sec. This water is being monitored, but it is not expected that acid drainage will occur during the life of the mine. Final decommissioning will involve sealing and flooding of the underground workings.

Figure 2 shows the acid-base relationship for waste rock and tailings from a major gold prospect in New Zealand. Four basic waste types are identified by this plot as acid forming, potentially acid forming, non-acid forming and barren.

The non-acid material has a negative NAPP and can be used as general fill or cover for engineering works. The barren waste rock is essentially devoid of sulphides and also has a low ANC. This material plots at the intersection of NAPP=0 line and the ANC=0 line. The barren waste can be used for any construction purposes providing its engineering properties are suitable.

An important consideration in material classified as non-acid is that selective dissolution and leaching of carbonates may eventually lower the ANC resulting in long term acid generation. However, this is only likely to occur where the sulphur level is greater than 2 or 3 percent.

Integrated geological and geochemical investigations show that approximately two-thirds of the waste rock and all the tailings fall into the acid forming and potentially acid zones. The natural pH of the potentially acid forming material is greater than 5 but since it has a positive NAPP there is a potential for acid generation and establishment of low pH conditions (ie. pH less than 4) after a period of oxidized leaching. The period of oxidized leaching required to generate acid conditions increases as the ANC increases (ie. as the lag period increases). Also, the potential scale of acid generation increases with increasing sulphur content.

Detailed mineralogical and leaching tests carried out on the potentially acid forming waste material has shown that acid conditions will not occur unless the material is exposed to oxidized leaching for at least 2 years. At this operation, waste materials have been classified according to geotechnical and geochemical characteristics. The waste disposal strategy has been designed to place acid forming and potentially acid forming material in cells which are constructed as 'sealed' units using non-acid, barren and soft argilic acid forming material as cell walls and cover. The soft argilic material can be used as intermediate cover since it can be compacted to high density and very low permeability. In addition, the mineralogical studies show that the clay matrix effectively isolates the sulphides thus minimizing exposure to oxidized leaching.

The tailings generated by processing operations in the two gas studies presented are classified as potentially acid forming. The base metal sulphide tailings contain approximately 30% sulphur whereas the gold tailings contain approximately 2% S. For control of acid formation it is essential that oxidized leaching of the tailings is prevented. Both tailings require a long period of exposure before acid formation is likely to occur and since both sites are in wet environments the long term rehabilitation strategy is to saturate the tailings and store under permanent water cover. The tailings dam walls are designed as water-retaining structures and the disposal strategies are aimed at providing maximum stability to the dam wall. It is considered that storage under water is the most effective way of preventing long-term acid formation in these waste materials.

CONCLUSIONS

The approach presented in this paper for determining the acid-forming characteristics of waste rock, tailings and mine rock has been applied to a wide range of base metal sulphide and gold mining operations. Acid-base analysis is an essential tool in the investigation strategy but the interpretation of the results and, most importantly, the engineering implications for waste management, pollution control and rehabilitation, must be carefully considered. Sampling and laboratory testing programs must be planned on a site-by-site basis and the acid-base analysis must be applied on individual samples rather than composite samples.

Once the geochemical waste types have been identified at a particular mine operation it is essential that a simple monitoring procedure be developed for the operation phase. In some situations a simple pH determination or visual inspection is all that is required. In others it may be necessary to determine pH and ANC while the complete NAPP and pH determinations may be necessary at difficult sites. In any mining situation it is generally best to attempt to limit the number of waste types to 3 or 4, otherwise scheduling difficulties could result in problems for reclamation, pollution control and decommissioning.

It is essential to communicate with the design and operation personnel since the success of acid mine drainage control and prevention of acid soil problems for reclamation will depend on the incorporation of geochemical factors into the scheduling and management of the waste materials. Numerous alternatives to the acid-base procedure and have been devised and are presented in the literature. However, from a practical point of view, in relation to the control of acid problems through implementation of selective material placement and dump design, we believe the acid-base procedure along with experienced interpretation is an effective and applied approach.

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A STUDY OF MINE DRAINAGE QUALITY AND PREDICTION USING OVERBURDEN ANALYSIS AND PALEOENVIRONMENTAL RECONSTRUCTIONS, FAYETTE COUNTY, PENNSYLVANIA[1]

Keith B. C. Brady, James R. Shaulis and
Viktoras W. Skema[2]

Abstract.--The Stony Fork watershed is a 7.44-mi^2 drainage basin in Fayette County, PA. Geologic investigations during the late 1970's established that surface mining in the watershed was largely limited to the Upper Kittanning coal seam. Interpretations of drill logs and field work has shown the Upper Kittanning and its overburden were deposited in an upper delta plain environment. This environment is marked by lateral variability and abrupt facies changes. This variability affects the distribution of calcareous materials, which is evident in acid-base account overburden data, and in the water quality associated with individual mine sites. Some mines are producing alkaline water while others are producing acid mine drainage. In addition to the paleoenvironmental controls on the distribution of calcareous strata, it was found that all overburden holes less than 40 ft. to the base of the Upper Kittanning coal lacked calcareous material. This absence is attributed to weathering. Sulfur on the other hand persists even at very shallow cover. Mine drainage quality is related to the presence or absence of calcareous rocks. Surface mining in areas devoid of calcareous rocks due to nondeposition or weathering has resulted in acid mine drainage. Mines developed in areas of abundant limestone produce alkaline water.

INTRODUCTION

The Stony Fork watershed, a 7.44-mi^2 drainage basin, is located in the Fort Necessity quadrangle in southern Fayette County, Pennsylvania. It is classified as a High Quality stream according to Pennsylvania Department of Environmental Resources (DER) Rules and Regulations and has been afforded special protection status since the early 1970's. Because of this status, a large amount of hydrologic and geologic information has been obtained from the applications for surface mines. Initially, these data were difficult to interpret. Results of overburden and water quality testing from mine sites in close proximity showed considerable variability. These differences were at first attributed to the presence of several coals in the area having dissimilar overburden characteristics. However, attempts at correlating these coals became very confusing. It soon became apparent that a much better understanding of the basic geology of the area was needed.

This was clearly understood by the late 1970's when Pennsylvania's Bureau of Forestry and Bureau of Topographic and Geological Survey were working in the area to develop an estimate of coal resources. In order to resolve the coal correlation problems, a series of deep exploration core holes were drilled. The cores were examined in detail, with special care given to identifying the key beds in the stratigraphic succession, ranging from the Conemaugh Group marine beds downward to the Mauch Chunk Formation red beds. As a result, an accurate stratigraphic framework was developed and a better understanding of the sedimentological characteristics of the area was achieved. It became evident that: (1) surface mining in the Stony Fork watershed is generally limited to a single coal seam, the Upper Kittanning; and (2) the variability of mine drainage, both alkaline and acid within a relatively short distance, is due to complex lateral changes in the Upper Kittanning overburden. This study attempts to relate the geologic features of the area to the quality of water produced during mining. It is hoped that a better understanding of these relationships will enhance predictability of potential problem areas and aid in preparation of future surface mining plans.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and the U.S. Department of Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988.

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METHODS

Forty test holes used for overburden analysis were obtained from the Bureau of Mining and Reclamation (BMR) surface mine permit files. The overburden from these holes was analyzed using the acid-base accounting method (Sobek and others, 1978) which identifies potentially acid and alkaline producing strata. Figure 1 shows the distribution of the overburden drill holes as well as the five most recent areas of mining within the watershed. Areas A through D have acid-base account overburden data. Area E does not have acid-base account overburden data, but the geology has been studied in detail and it is included because of its proximity to the other mine sites.

Values for calcium carbonate equivalent and percent total sulfur were obtained from the overburden analysis test holes. The neutralization potential (NP) values for each sample were weighted according to thickness of each interval. These values were then multiplied by the weight of the sample stratum per acre foot. The resulting value for each hole is in terms of tons $CaCO_3$/acre. Likewise the maximum potential acidity (MPA) data were summed giving tons $CaCO_3$/acre deficiency for each drill hole. The traditional "excess" and "deficiency" (net NP plus MPA) as described by Sobek and others, 1978, were not used in this study. Included in the calculations were all overburden strata above the coal and one ft of the strata immediately below the coal. Coals were not included. Eight of the holes at Site A had NP determined on only those strata that "fizzed" when dilute hydrochloric acid was applied. Experience

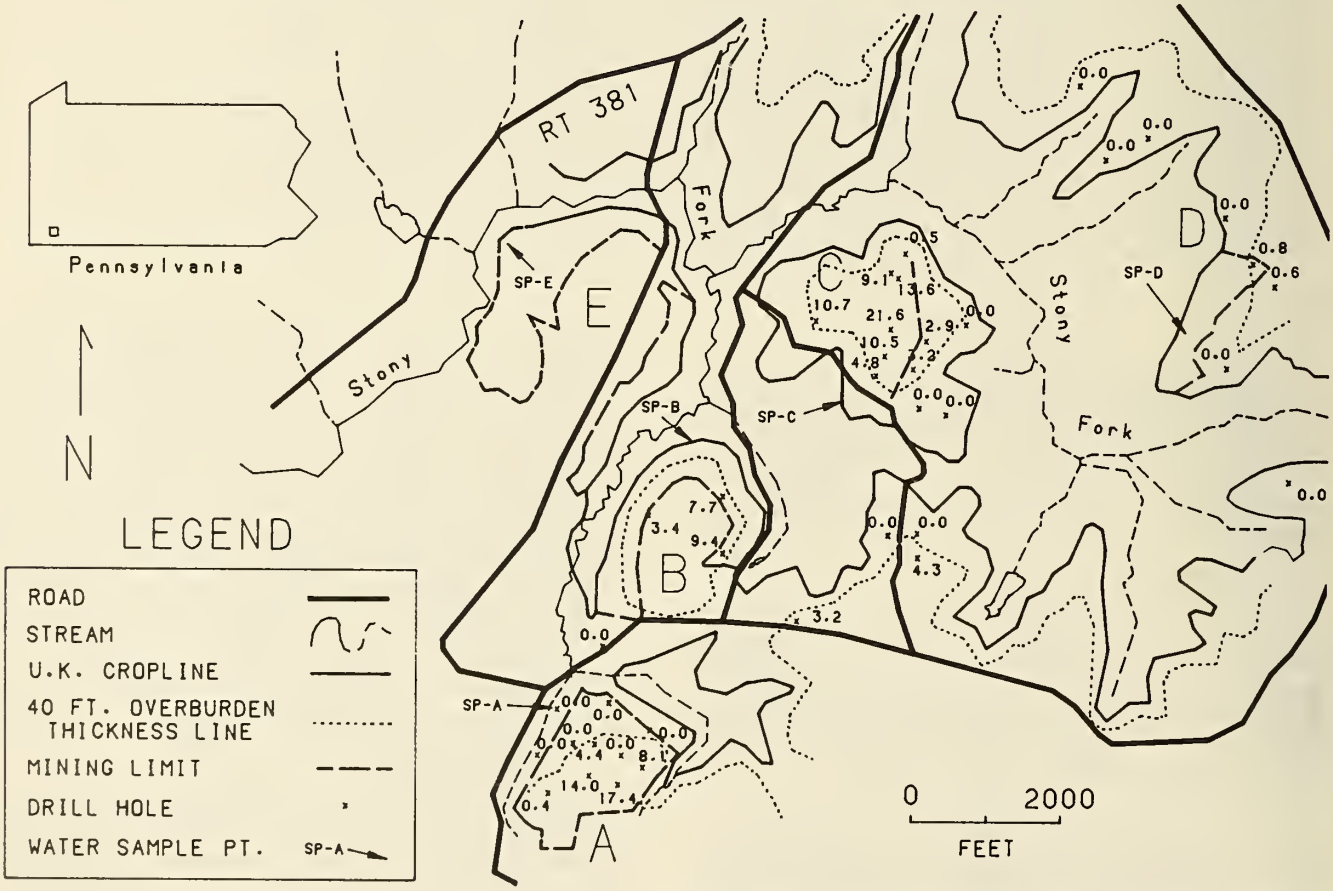

Figure 1.--Map of study area showing overburden analysis drill hole locations and associated mine sites (A through E). The numbers beside the drill hole locations indicate the amount of calcareous material in the hole presented as thousands of tons of $CaCO_3$ per acre. Note that all holes outside the 40 foot cover line have 0.0 amount of calcareous material.

has shown that rocks with NP's less than 30 do not normally exhibit a fizz, whereas rocks with NP's greater than 30 normally do. In order to include all data in our calculations and to make the data internally consistent, only NP's greater than 30 with a fizz were used. Experience has shown that NP's less than 30 do not generally contribute significant alkalinity and total sulfur values of less than 0.5 percent often do not result in poor quality water. Only sulfur values greater than 0.5 percent and neutralization potentials greater than 30 tons $CaCO_3$/1000 tons were used in the calculations. A comparison between these data versus data including all NP and sulfur values yielded similar results.

Water sample data used in this study were obtained from BMR permit files. The analyses include both BMR samples and company monitoring data.

Geologic cross sections and isopach maps were constructed to determine the thickness distribution and lateral and vertical relationships of the various rock units in the area. Additionally, a series of maps was drawn showing the areal distribution of rock types at different stratigraphic levels. These slices through the strata at arbitrary vertical positions are intended to show successive patterns of sediment deposition occurring throughout the area at different instances of time. This method of recreating contemporaneous depositional environments is an approximation. Differences in compaction of dissimilar sediments, downcutting of stream channels and original topographic relief are factors which distort precise time line reconstructions.

A wide range of types of data was used for developing the geologic cross sections and maps. Reliability of information used was generally very good. Most of it consisted of geologists' descriptions of cored exploration drill holes, overburden test hole logs, and surface mine highwalls. This was supplemented by the somewhat less reliable descriptions of rock cuttings from air rotary drill holes submitted with mining permit applications. The data points used in the construction of cross-sections, isopach maps and lithology distribution maps are shown in figure 2.

GENERAL GEOLOGY

The stratigraphic section examined in this study consists of the stratigraphic interval from 20 ft below to 100 ft above the Upper Kittanning coal. It ranges from the calcareous rocks associated with the Johnstown limestone at the bottom of the section, to the rocks overlying the Upper Freeport coal horizon at the top (figs. 3 & 4). The prominent feature throughout this section is the laterally discontinuous nature of the rock units. Correlation of these units is difficult, and an essential first step in understanding their lateral relationship is construction of a stratigraphic framework. This was accomplished by correlating the persistent marine zones found in the lower part of the overlying Conemaugh Group. The Brush Creek, Pine Creek, and Woods Run marine zones are persistent throughout the area and were recognized in every drill hole that penetrated their horizons (fig. 5). The first red beds encountered in the upper part of the Mauch Chunk Formation also provided useful stratigraphic control from below.

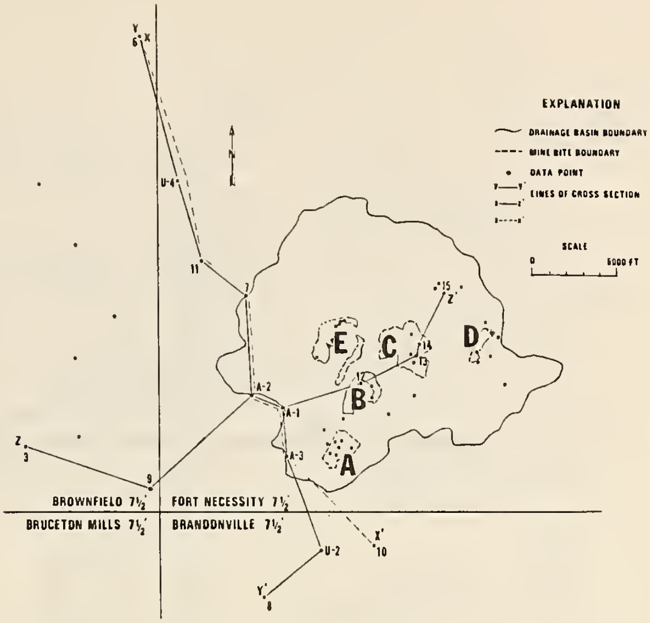

Figure 2.--Data and section line location map. Bold letters (A-E) designate mine sites discussed in text.

Sedimentologically the prominent features in this study are the Upper Kittanning coal, a sandstone overlying the coal, and several calcareous beds. The Upper Kittanning Coal is generally thick and continuous over most of the area (fig. 6). Several splits of the coal are apparent in section Y-Y' (fig. 3). One occurs in the area of holes 7 and 11. The coal here is split by a sandy siltstone wedge which becomes thicker and coarser to the west. On the southern end of section Y-Y' (Hole 8) a 2.5-ft argillaceous limestone parting in the coal suggests splitting in a southward direction.

The sandstone overlying the coal in the western part of the drainage basin has a lenticular, elongate shape. The thicker part of this lense is approximately a mile wide in the south and narrows to less than a half mile wide northward (fig. 7). The sandstone is coarse-grained at the base and becomes fine-grained upward. The thick, main body of the sandstone grades laterally into thin, very fine-grained sandstones interbedded with sandy silt shales, silty clay shales, and calcareous silty claystones.

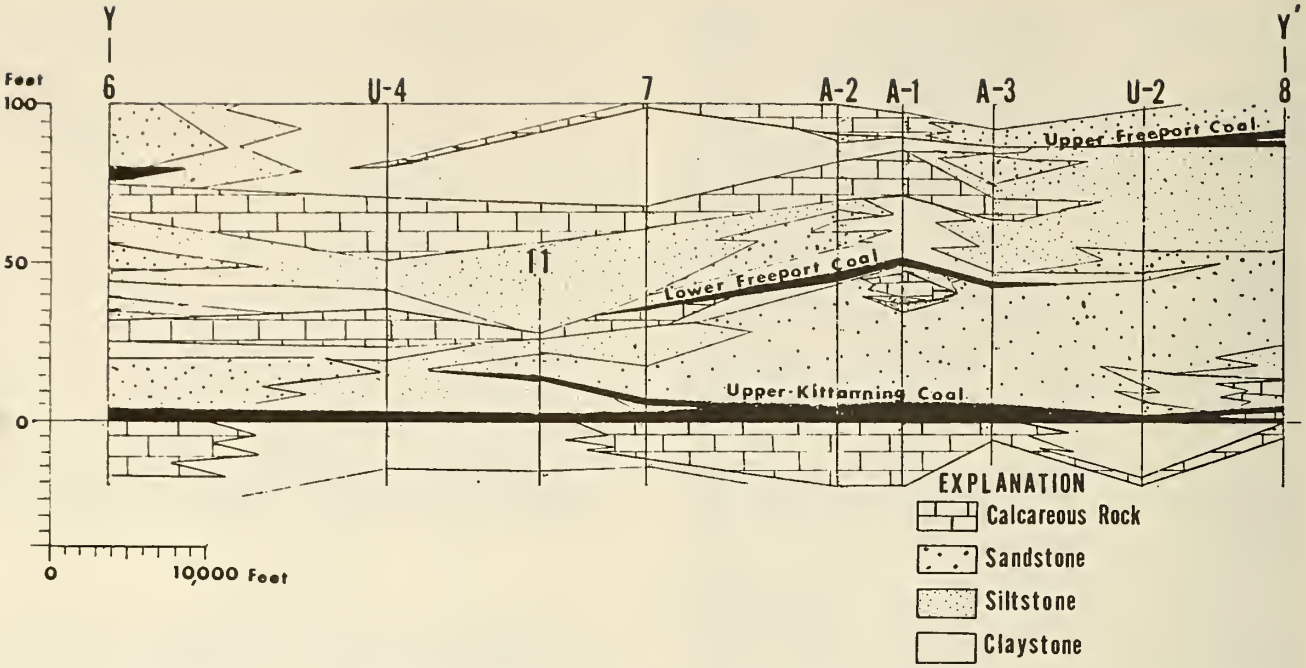
Y
Y'
Feet
100
50
0
6
U-4
7
A-2
A-1
A-3
U-2
8
11
Upper Freeport Coal
Lower Freeport Coal
Upper Kittanning Coal
0
10,000 Feet
EXPLANATION
Calcareous Rock
Sandstone
Siltstone
Claystone

Figure 3.--Stratigraphic cross section (Y-Y') of the Upper Kittanning to Upper Freeport interval.

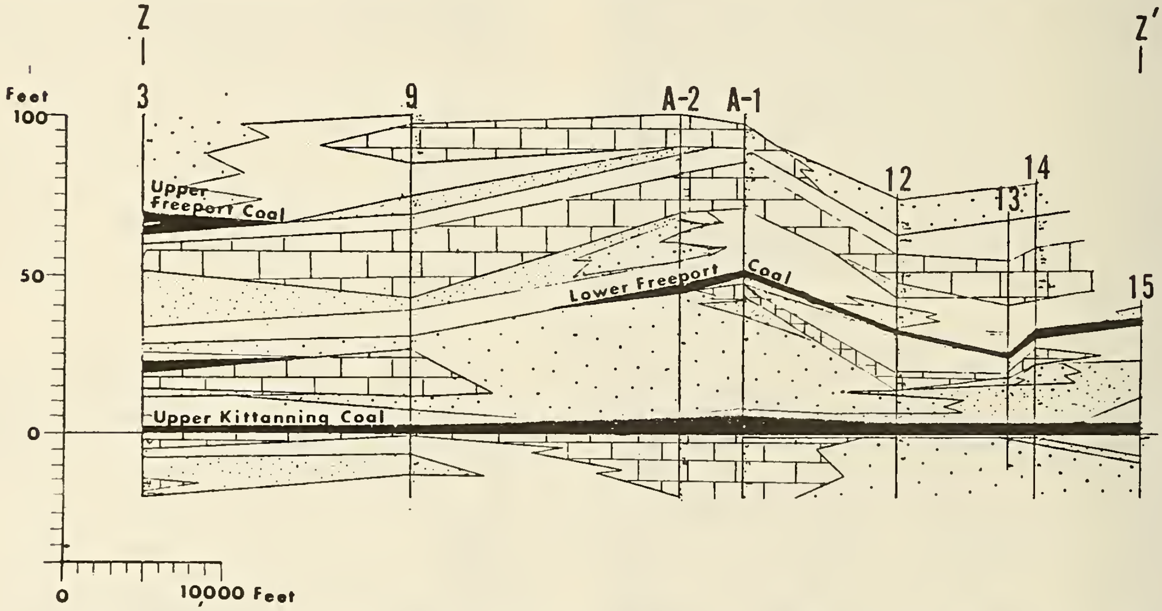
Z
Z'
Feet
100
50
0
3
9
A-2
A-1
12
13
14
15
Upper Freeport Coal
Lower Freeport Coal
Upper Kittanning Coal
0
10000 Feet

Figure 4.--Stratigraphic cross section (Z-Z') of the Upper Kittanning to Lower Freeport interval.

This part of the section also has three, discrete, major calcareous zones. These zones often contain argillaceous limestones and contain freshwater fossils (Spirorbis and ostracodes). The most persistent and thickest of these is beneath the Upper Freeport coal horizon approximately 50 to 80 ft above the Upper Kittanning coal (figs. 3 & 4). Another thick but discontinuous zone is present below the Upper Kittanning in the western part of the area. This calcareous zone attains a maximum thickness of 25 ft and usually contains the argillaceous Johnstown limestone. The area where the limestone is thickest and least argillaceous coincides with the thickest development of the Upper Kittanning coal and overlying sandstone. South of the Stony Fork drainage basin this calcareous zone appears to be laterally equivalent to the Upper Kittanning coal. Limestone in drill hole 8 is found directly below and above the coal and forms a thick parting in the coal itself (fig. 3). A few small isolated pods of limestone directly on top of the coal were encountered at other locations in and around the basin. A third major calcareous zone is situated approximately 15 to 40 ft above the Upper Kittanning coal. Its position varies from just below the Lower Freeport coal horizon to midway between the Lower Freeport and

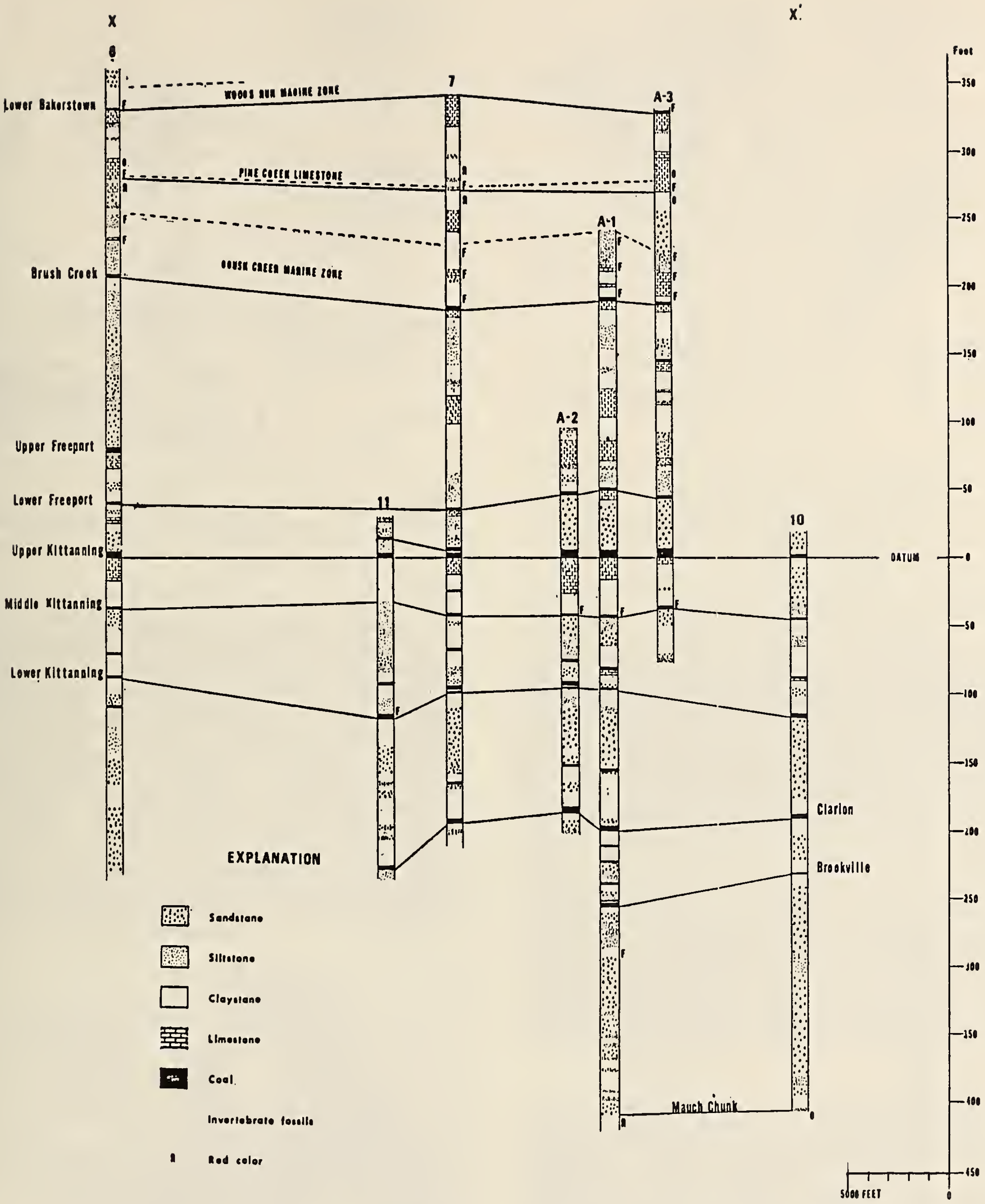
X
X'
8
7
A-3
A-1
A-2
11
10
Lower Bakerstown
WOODS RUN MARINE ZONE
PINE CREEK LIMESTONE
BRUSH CREEK MARINE ZONE
Brush Creek
Upper Freeport
Lower Freeport
Upper Kittanning
Middle Kittanning
Lower Kittanning
Clarion
Brookville
Mauch Chunk
DATUM
Feet
350
300
250
200
150
100
50
0
50
100
150
200
250
300
350
400
450
5000 FEET
0
EXPLANATION
Sandstone
Siltstone
Claystone
Limestone
Coal
Invertebrate fossils
Red color
F
R

Figure 5.--Stratigraphic cross section of the Mauch Chunk Formation to Lower Bakerstown coal interval. See figure 2 for location of section.

Upper Kittanning.

In addition to the well-developed Upper Kittanning coal, two other coals of minor significance are present in and around the drainage basin. The Lower Freeport coal has a sporadic distribution in the study area. It reaches a maximum thickness of 2 to 3 ft, but is thin to absent over much of the area. The Upper Freeport coal is rarely present in the study area. Carbonaceous clay shales, calcareous claystones, and argillaceous limestones containing fossil ostracodes and *Spirorbis* often occupy its horizon.

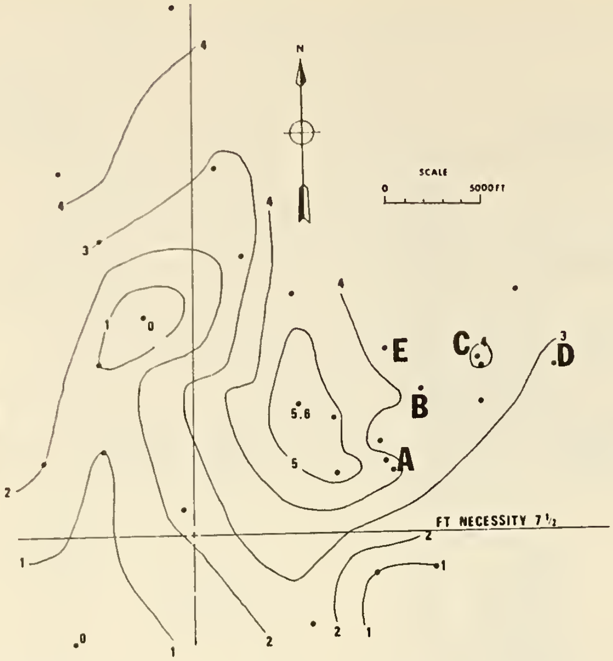

Figure 6.--Thickness map of the Upper Kittanning coal. Thickness lines given in feet.

PALEOGEOGRAPHY

The map showing distribution of lithologies 1 ft below the Upper Kittanning coal indicates the presence of a large body of sandstone in the eastern portion of the study area (fig. 8). Not enough information is present to determine its gross geometry, however a few deep holes indicate that the sandstone which is as much as 40 ft thick grades upward from coarse to very fine-grained. It is adjacent to a narrow belt of claystone to the west which separates the sandstone from a large area of calcareous claystone and argillaceous limestone containing fossil freshwater invertebrates. These calcareous deposits are indicative of a freshwater lake or pond environment. The narrow belt of claystone and adjacent very fine grained upper part of the sandstone body suggest the presence of overbank deposits flanking a levee and stream channel system to the east.

This period of time appears to be followed by a nearly complete cessation of deposition over the entire study area, and the subsequent development of luxuriant vegetation of the Upper Kittanning peat swamp. Some local ponding of water too deep to sustain vegetation occurred in the swamp complex. This resulted in the formation of the limestone partings seen in several places. The coal split located in the area of drill holes 7 and 11 may indicate the presence of a brief very local incursion of sediment into the peat swamp from the north-west (fig. 3). Closer spacing of drill holes is needed in this area to better understand this minor episode of deposition.

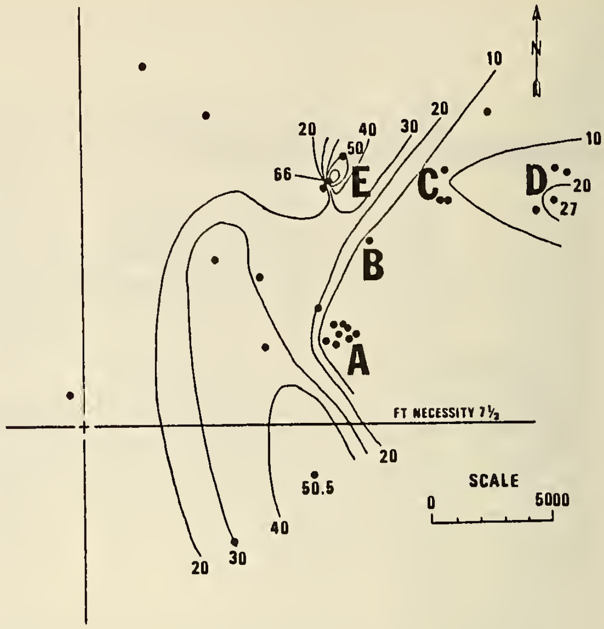

Figure 7.--Thickness of the sandstone above the Upper Kittanning coal. Thickness lines given in feet.

Distribution of lithologies 10 ft and 25 ft above the coal provide a good look at the nature of the sediment influx which terminated Upper Kittanning peat development (figs. 9 and 10). Initially a blanket of sand and silt was deposited over the peat throughout most of the area. A fluvial channel oriented roughly north-south (fig. 7) and associated levee deposits were soon established in the area underlain by the thickest coal and limestone. In the early stages of sediment influx over the peat swamp this area of thick peat would probably have undergone the most compaction and would have quickly localized the channelway. As a result,

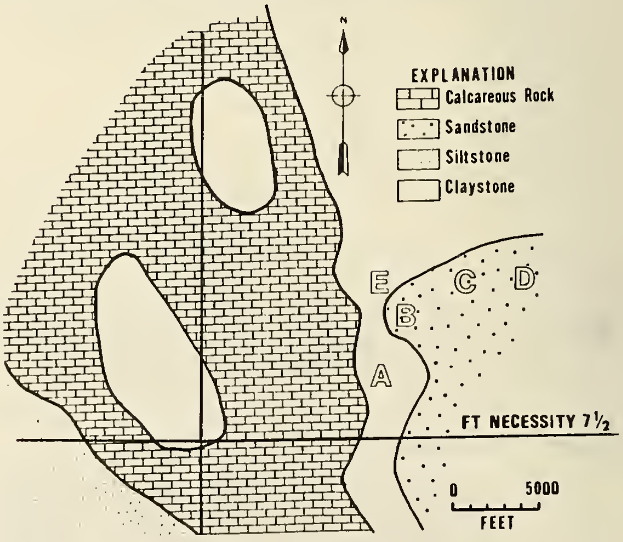

Figure 8.--Distribution of lithologies one foot below the Upper Kittanning Coal. Letters designate mine site locations.

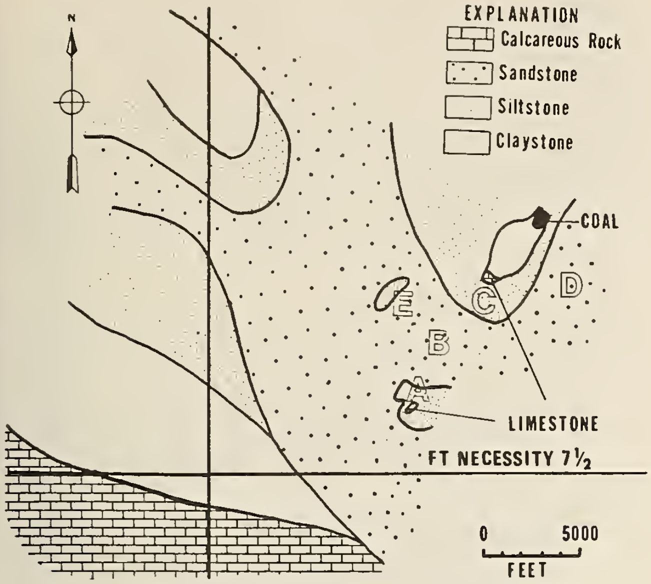
N
EXPLANATION
Calcareous Rock
Sandstone
Siltstone
Claystone
COAL
D
E
C
B
A
LIMESTONE
FT NECESSITY 7½
0
5000
FEET

Figure 9.--Distribution of lithologies 10 feet above the Upper Kittanning coal. Letters designate mine site locations.

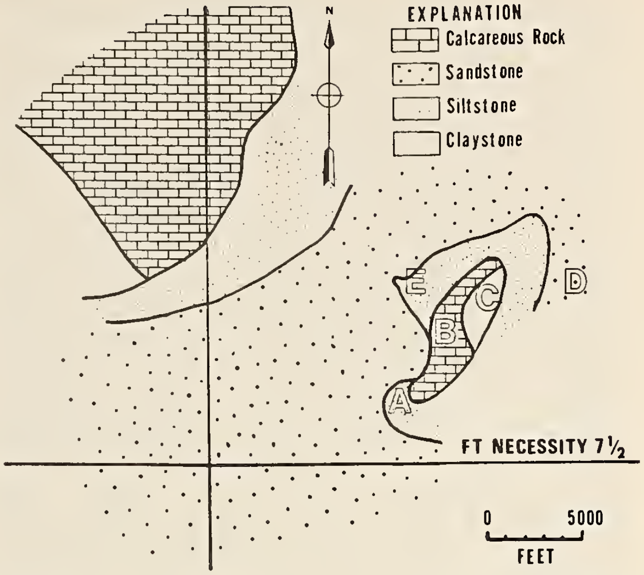
N
EXPLANATION
Calcareous Rock
Sandstone
Siltstone
Claystone
E
C
D
B
A
FT NECESSITY 7½
0
5000
FEET

Figure 10.--Distribution of lithologies 25 feet above the Upper Kittanning coal. Letters designate mine site locations.

ponded overbank areas of very low energy were established soon after flooding of the swamp. Calcareous claystones, such as the ones found in the overburden of mine sites A and C were being deposited in close proximity to the high energy channel system (fig. 9). The area between mine sites A and C just to the east of the channel developed into a persistent site of low energy (figs. 10 and 11). By the time the sediments 50 ft above the coal were deposited the main channel area appears to have lost much energy and become very narrow (fig. 11). The major episode of ponding which was to cover the entire area with calcareous deposits by Upper Freeport time, was just beginning in the western part of the study area.

The map of rock distribution 10 ft above the coal shows an area in the northeastern part of the Stony Fork watershed in which thin coal is present (fig. 9). This is an area where considerable splitting of the Upper Kittanning coal has been observed in mining. It is just west of an area containing relatively thick very coarse grained sandstone with some granular size grains. This could indicate the presence of a channel system contemporaneous with the peat swamp to the east. This channel system may be related to the sandstone body found directly under the coal in the eastern portion of the study area (fig. 8).

In summary, considering the relatively narrow width of the stream channel system and adjoining levees, and the preponderance of freshwater lake and pond sediments throughout the section, this area was most probably part of an interdistributary area of an upper delta plain during Upper Kittanning to Upper Freeport time. Except for some clays, these areas received little sediment input; as a result aggradation could not keep up with subsidence, and small water bodies were formed. The development and enlargement of these ponds drowned out the peat-producing marshes and swamps. Streams carrying a sandy bed load in this type of environment can be expected to be small and sinuous (Frazier and Osanik, 1969). As a result patterns of deposition within this environment are complex with many lateral changes.

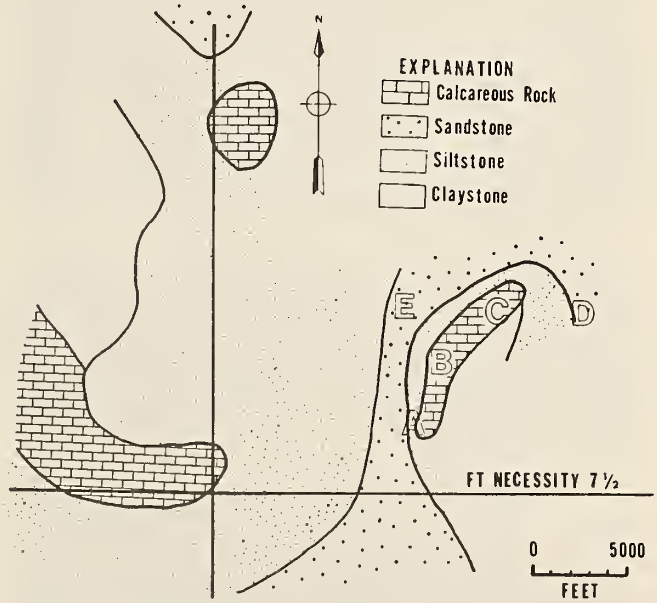
N
EXPLANATION
Calcareous Rock
Sandstone
Siltstone
Claystone
E
C
D
B
A
FT NECESSITY 7½
0
5000
FEET

Figure 11.--Distribution of lithologies 50 feet above the Upper Kittanning coal. Letters designate mine site locations.

DISTRIBUTION OF NEUTRALIZATION POTENTIALS AND SULFUR AS THEY RELATE TO WEATHERING

In this area there is a weathering profile to a depth of 20 feet below the surface which has selectively affected the calcareous rocks and pyrite concentrations of the Upper Kittanning overburden in the study area. Field observations and drilling records have reported brown to orange coloration of the rocks and soil in this interval. The effects of weathering on $CaCO_3$ can be seen in the NP data gathered for the study area. A plot of the NP data in terms of tons $CaCO_3$ per acre ft versus thickness of overburden on the Upper Kittanning coal seam in figure 12 clearly shows a $CaCO_3$ threshold at a thickness of about 40 ft. Holes that encountered less than 40 ft of Upper Kittanning overburden lack calcareous material. Holes that penetrated more than 40 ft of Upper Kittanning overburden show a wide range of values, from 0 to hundreds of tons $CaCO_3$/acre ft. There are two reasons for this. In the first place, test holes in the study area show that significant occurrences of limestone are usually found 20 ft or more above the Upper Kittanning coal seam (figs. 3 & 4). In the second place, weathering has leached all the carbonate material to a depth of 20 ft below the surface. Because of these two factors, more than 40 ft of Upper Kittanning overburden is required before any measurable amounts of $CaCO_3$ can be found. If the effects of weathering were eliminated overburden thicknesses of only 20 ft could have calcareous material present. Figure 13 is a plot of sulfur versus thickness of Upper Kittanning overburden (sulfur is expressed in terms of tons $CaCO_3$ deficiency/acre ft). Unlike the calcareous material, the sulfur data shows no overburden thickness threshold. Sulfur greater than 1.0 percent was present at depths of only 10 to 15 ft below the surface. It appears that weathering of $CaCO_3$ is more complete than weathering of pyrite at shallow depths. Therefore, areas within the Stony Fork watershed with less than 40 ft of overburden will lack calcareous material, but still potentially have high sulfur concentrations.

Figure 12 shows that when there is more than 40 ft of overburden there is a wide range in available alkaline material. We attribute this to the regional and patchy distribution of freshwater limestone and occasional fluvial channels cutting out and replacing the limestone with non-calcareous rocks.

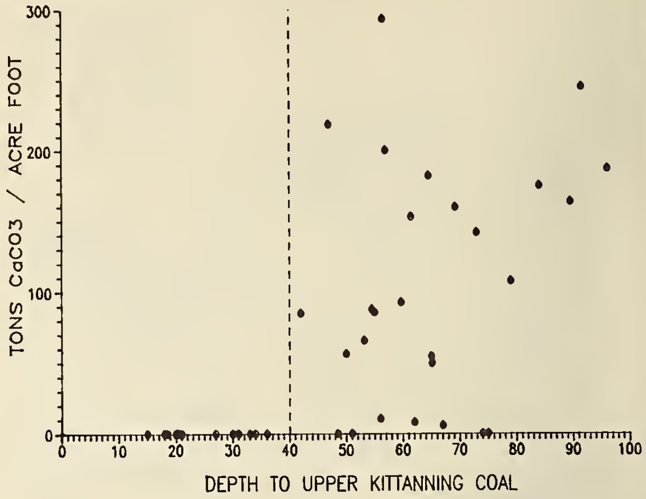

Figure 12.--Graph showing relationship between calcareous material per acre foot and depth to bottom of Upper Kittanning coal. calculations were made based on neutralization potentials above 30 tons/1000 tons.

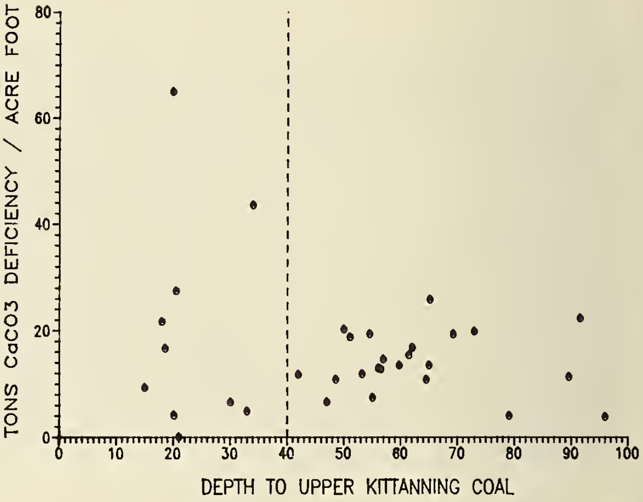

Figure 13.--Graph showing relationship between potentially acid producing strata and depth to bottom of Upper Kittanning coal. Calculations were made based on sulfur values above 0.5%.

WATER QUALITY OF MINE SITES

In each of the five mine sites studied (A through E) the Upper Kittanning coal was the principal seam of interest. The Lower Freeport coal horizon was also encountered at each site but generally appeared as a thin coal or a carbonaceous shale except at site C where it reached a minable thickness. Calcareous rocks where present consisted of either argillaceous limestone or claystone with limestone nodules. The maximum highwall heights ranged from a low at site D of 45 ft to a high at sites A and C of 90 ft.

Determinations of water quality were made on pit water samples taken during mining, and on water from crop springs, monitoring wells, and spoil seeps taken both during and after mining. These samples were analyzed for pH, alkalinity, acidity, iron, manganese, aluminum, and sulfate. Summaries of selected parameters are shown in tables 1 and 2.

TABLE 1. -- PIT WATER DURING ACTIVE MINING

Mine Site	N	pH			Net Acidity[1] mg/l			Sulfate mg/l		
		Med.	Q1[2]	Q3	Med.	Q1	Q3	Med.	Q1	Q3
A	14	6.7	6.2	7.0	-68	-85	-34	101	43	166
B	6	6.0	5.4	6.6	16	-15	59	17	6	29
C	2	7.2	7.1	7.3	-154	-224	-84	79	59	99
D	19	3.0	2.0	3.1	406	250	1028	630	420	900
E	9	3.3	3.1	3.8	158	65	194	380	250	592

[1] Net acidity = acidity - alkalinity. Negative number indicates net alkalinity.
[2] Q1 and Q3, upper and lower quartilies determined by sorting

TABLE 2. -- POSTMINING WATER QUALITY

Sample Point	N	pH			Net Acidity[1] mg/l			Sulfate mg/l		
		Med.	Q1[2]	Q3	Med.	Q1	Q3	Med.[3]	Q1	Q3
SP-A					see figure 14 graph					
SP-B	4	5.6	5.5	5.8	6.0	0.2	11.8	<43	-	-
SP-C	7	6.0	5.7	6.3	-4	-34	4	<40	-	-
SP-D	9	3.2	3.0	4.2	456	293	609	918	756	1040
SP-E	4	2.8	2.7	2.9	988	796	1154	1281	1112	1545

[1] Net acidity = acidity - alkalinity. Negative number indicates net alkalinity.
[2] Q1 and Q3, upper and lower quartilies determined by sorting.
[3] Less than symbol, "<" indicate that some lab values reported as "<40 mg/l" SO_4

Mine site A was activated in early 1985 and was nearing completion at the time of this writing. It occurs in an area of paleoenvironmental transition. The mine site encompasses both the coarser clastic sediments associated with the distributary channel system located in the west and the lower-energy overbank sediments, including limestones to the east. The effects of this transition are reflected in the overburden analyses and in the water quality associated with this site. Three alkaline zones were encountered at 2-10 ft, 20-25 ft, and 50-65 ft above the Upper Kittanning coal. This operation had a maximum overburden height of 85-90 ft. These zones occur as lenticular bodies that are very limited in their lateral extent. The lowest alkaline zone was an 8 ft thick lenticular parting at the top of the Upper Kittanning coal occupying an area of only about 20,000 ft^2. Some test holes starting 70 ft above the Upper Kittanning coal had little or no alkaline material present. Analysis of pit water samples have been consistently alkaline, although sulfate showed a general increase through time indicating the presence of both alkaline and acid-producing rocks. A down gradient monitoring well below the earliest backfilled area has begun to show a rise in sulfate and metals (fig. 14). The precise cause of this will require further investigation, however, some possible explanations include an insufficient amount of alkaline material present to inhibit pyrite oxidation or more acid-producing material present than anticipated. Further monitoring will be necessary to determine whether the increases in concentration are a persisting trend or a short term fluctuation.

Mining at site B was initiated in July 1983 and was completed by October 1984. The geology at mine site B is similar to mine site A. The depositional environment of the overburden rocks in the western most part of the site was the same distributary channel system found in site A. Overburden in this area consisted primarily of sandstone for a distance of 50 ft above the Upper Kittanning coal. Eastward the sandstone thinned abruptly and silts, clays and calcareous sediments were deposited in a low energy overbank environment. Two main alkaline bearing zones were found 15-20 ft and 50-60 ft above the Upper Kittanning Coal seam which was mined to a maximum highwall height of 70 ft. The two alkaline zones were found to be persistent throughout the site except in the extreme western edge. The pit water contained low concentrations of sulfate and metals and ranged from weakly acidic to weakly alkaline. Sample SP-B (table 2) from a crop spring is weakly acidic with low concentrations of sulfate and metals. The pit water at mine site B and the crop spring sample SP-B show virtually no impact from mining. Normally postmining water quality will show an increase in dissolved solids. The water quality in the deeper portions of the mine site where the rock/water contact time is greatest may not be reflected at sample point SP-B. It may be that SP-B only reflects shallow flow from the periphery of the mine site.

Mine site C was first started in January 1985 and is active at the time of this writing. Mine Site C is located almost entirely in a low energy depositional environment marked by extensive deposition of limestone and calcareous strata. As in site A three alkaline bearing zones were present at 5-10 ft, 20-25 ft and 50-60 ft above the Upper Kittanning coal seam, and the site also had a maximum overburden of 85 to 90 ft. Unlike site A however, the upper two limestone zones were found to be laterally persistent over the entire site. Also, unlike site A or B, the Lower Freeport coal was of sufficient thickness to be a minable seam. The pit water was highly alkaline with low sulfate and metals concentrations due to the abundance of alkaline rock strata present. A low flow seep, SP-C (table 2), developed below a backfilled portion of the site, is characterized as mildly alkaline, low sulfate, with metals concentration slightly above background. Because this site is still active, a full evaluation of postmining water quality is not possible and will not be until the ground water regime reestablishes itself. Seep SP-C probably represents relatively shallow flow of short retention time. Of the sites discussed this mine will encounter the largest quantity of alkaline-bearing strata due to the persistence of the calcareous zones and the large area above 40 ft of cover. It is anticipated that the alkaline material will be sufficient to prevent postmining water quality problems.

Mine site D was activated in late 1979, with mining on the decline by late

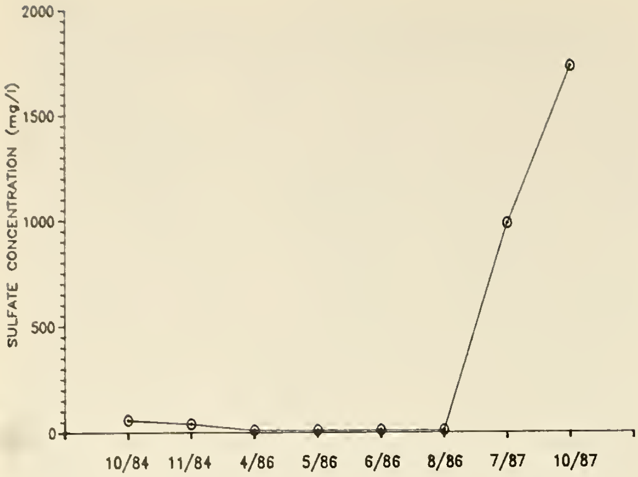

Figure 14.--Graph of Mine Site A monitoring well sulfate concentrations through time.

1981. The site has now been abandoned and has been left unreclaimed. Mine site D is located in a high energy depositional environment. This is suggested by the presence of thick coarse grained sandstone overlying the coal, a lack of calcareous strata and numerous claystone partings and boney layers in the coal. No alkaline bearing rocks were found in the overburden which reached a maximum height above the Upper Kittanning coal of 40 to 45 ft. In this site the Upper Kittanning coal uncharacteristically contains numerous carbonaceous, pyritic claystone partings sometimes as great as 2 ft in thickness. The Lower Freeport coal was generally thin to absent over the entire site except for a several acre area where it reached a minable thickness. Pit waters during mining were highly acidic with high sulfate and metals concentrations (table 1). Seeps which developed along the toe of spoil are of even poorer water quality. This quality of water is attributable to the lack of calcareous material and the indiscriminate spoiling of substantial quantities of carbonaceous, pyritic claystone partings.

Mine site E was actively mined from 1979 to 1981, when it was abandoned; it remains unreclaimed. The overburden rocks of mine site E were deposited in the north-south trending distributary channel system seen also on the western edges of mine sites A and B. Thick massive sandstones deposited in the main channel and steeply dipping interbedded siltstones and sandstones associated with point bars are the predominant rock types found over much of the site. These high energy environment deposits persist throughout the overburden as high as 85 ft above the Upper Kittanning coal. No alkaline-bearing zones were found in the Upper Kittanning overburden. As in Site D the Lower Freeport coal was generally thin or absent, except in a very small area where it became thick enough to be minable. Pit water was always of poor quality with low pH and high acidity and sulfate (table 1). Toe of spoil seeps display similar but somewhat poorer water quality characteristics (sample SP-E, table 2). In addition a pre-existing Upper Kittanning country bank deep mine 500 ft south of SP-E also showed a deterioration in water quality during active mining (Stump and Mastrilli, 1985) and continues to be degraded.

SUMMARY AND CONCLUSIONS

Based on the foregoing study of the Stony Fork watershed, the following conclusions can be made:

1) The distribution of alkaline material is the primary control on mine drainage quality. Areas lacking alkaline strata produce acid mine drainage; areas with significant alkaline strata produce alkaline water.

2) Areas where the Upper Kittanning overburden is less than 40 ft thick are devoid of alkaline material due to weathering of the alkaline zone that occurs approximately 20 feet above the coal. High sulfur content, however, occurs within strata as shallow as 10 to 15 ft from the surface. Therefore,a zone from the cropline to a 40 ft overburden thickness line lacks alkaline strata, but sulfur bearing strata still persist within this zone. Consequently, mines developed in overburden of 40 ft or less will most likely produce acid mine drainage.

3) The Upper Kittanning and Lower Freeport coals and overburden were deposited in an upper delta plain interdistributary environment. This environment is marked by narrow stream channel systems and freshwater lakes and ponds. Mine sites developed in or adjacent to the high energy paleostream channels lack calcareous materials. Coals in these areas often contain claystone partings and boney layers. Mine sites located in low energy areas away from the channels are marked by extensive calcareous deposits. Because of this variability an upper delta plain environment does not necessarily ensure good quality water.

4) Mines developed in areas of high energy depositional environments are acid mine drainage producing whereas mines developed in areas of low energy depositional environments are alkaline producing. The exception to this would be mines of low cover in low energy depositional environments that

would be acid producing due to weathering of calcium carbonate.

5) In areas of significant paleoenvironmental variability, adjacent mining cannot be relied upon as a mine drainage quality predictor. Site-specific overburden analyses are important for delineating the distribution of alkaline and acidic materials.

6) Pit water quality in a broad sense appears to be a fairly good indicator of postmining water quality,although pit water quality is generally lower in metals and sulfate concentrations.

7) Mining plans should be designed such that sufficient alkaline material will be encountered. In the Stony Fork study area thickest Upper Kittanning coal development tends to coincide with areas which have the thickest sandstone overburden and which lack alkaline material. However, the coal in these areas tends to be underlain by thick limestone. A possible mining plan in these cases would involve deepening the pit in order to incorporate the underlying limestone into the spoil. In other instances when alkaline material does occur in the overburden, but only under high cover, the cuts could be run perpendicular to contour in order to blend the alkaline material evenly throughout the backfill.

ACKNOWLEDGMENTS

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LITERATURE CITED

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PHOSPHATIC CLAY SLURRIES FOR REDUCING ACID MINE DRAINAGE FROM RECLAIMED MINE SITES

Eric D. Chiado and Dr. John J. Bowders and Dr. John C. Sencindiver [1]

Abstract.-- Research at West Virginia University is being conducted on developing a phosphatic clay slurry seal that will prevent or reduce acid mine drainage produced from reclaimed sites. The spoil material that is used to reclaim sites in West Virginia consists primarily of shale and sandstone. When exposed to oxygen and water the spoil produces acid mine drainage. By developing an effective phosphatic clay slurry seal, it will be possible to hydrologically isolate the acid producing materials. An added benefit of this application is that phosphatic clay, which is a waste product of the production of fertilizer, will be utilized, thereby reducing the need for storage of these clay wastes. An effective way of hydrologically isolating the acid producting material is to reclaim sites using a layered system consisting of spoil material, overlain with a phosphatic clay slurry which is in turn overlain by cover soil. Current research is being conducted to define an optimum system that will produce the lowest permeability and reduce the acidity of any effluent generated in the acid materials. To date, laboratory permeability test results indicate that the compactive effort is the dominant variable in determining the permeability of the spoil-slurry system. Low water content slurries (150% to 250%) should be applied to uncompacted spoils, and high water content (250% to 350%) slurries should be applied to compacted spoils. The thickness of the slurry does not appear to significantly alter the permeability of the spoil-slurry system. The addition of the slurry has resulted in a 40 to 80 percent decrease in the permeability of the spoil material. The addition of slurry also dramatically decreases the concentrations of iron, manganeese, magnesium, aluminum, and sulfates in the effluent. Slight increases in the pH of the effluent were also demonstrated. Additional testing is underway to establish the optimal conditions for obtaining minimum permeabilities.

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In the past 50 years an ever increasing amount of research has been conducted on the control and remediation of acid mine drainage (AMD) produced from both deep and surface coal mines. Many of these efforts have concentrated on the use of crushed limestone or other base materials to neutralize the AMD. These methods, however, required perpetual reapplication to insure sufficient buffering capacity. Futhermore, the application of base materials could only neutralize the acid, but was unable to stop or prevent the acid producing reaction. The increasing environmental awareness of the public and the increasing cost of remediation has made it desirable for the coal mining industry to seek alternative methods for controlling AMD.

To this end, research is being conducted at West Virginia University on the use of phosphatic clay to control the formation of AMD. Phosphatic clay is the waste product of the production of fertilizer. Approximately 400 million tons of this waste are currently stockpiled in Florida, and this amount is expected to exceed 1 billion tons by the year 2000 (Lin). Using this waste product for the control of AMD will have the added benefit of reducing some of the disposal problems facing the phosphate fertilizer industry.

Phosphatic clay is made up of approximately 25% apatite, 60% smectitic clay minerals, and 15% various other phosphate minerals (Renton). The apatite consists of calcium phosphate ($Ca_5(PO_4)_3$), which becomes readily soluble below a pH of 7.0. This dissolution frees the phosphate ion, which has a strong affinity for metal ions. The smectitic clay minerals are composed primarily of montmorillonite. When exposed to water, montomorillonite expands several times its original volume, which results in a very low permeability. These two characteristics of phosphatic clay; the ability to release phosphate ions and low permeability, make it extremely attractive for use in controlling the formation of AMD.

It is generally accepted that the oxidation-hydrolysis of pyrite (FeS_2) contained in spoil material and coal refuse produces AMD. When pyrite is exposed to oxygen and water, it dissociates into ferrous ions (Fe^{+2}) and sulfate ions (SO_4^{-2}). The ferrous ion is futher oxidized to the ferric ion (Fe^{+3}). Once the ferric ion has been formed it takes over as the primary oxidizing agent, and these reactions do not stop until the pyrite supply is exhausted (Renton). As these reactions progress metals such as magnesium and aluminum, if present, can also be leached from the spoil. The end result from all of this chemical activity is AMD. The quality of AMD can range from low acidity with high concentrations of sulfates and low concentrations of metals, to AMD high in acidity, metals, and sulfates (Kleinmann).

The application of phosphatic clay to reclaimed mine sites has the ability to not only neutralize, but also completely stop this reaction (Renton). An efficient way to achieve this goal is to place a slurry of phosphatic clay over the potentially acid producing spoil. The montmorillonite provides a first line of defense in the form of a hydraulic seal against infiltrating surface water. Because of montmorillonite's low permeability, any surface water that is not eventually evaporated will require a great deal of time to pass through the seal. Any water that does manage to pass through the seal will react with any exposed pyrite. The resulting acidic environment will dissolve the calcium phosphate. The phosphate ions will react with the ferric and ferrous ions to form almost insoluble iron phosphates. The major oxidizing agent will be removed, and the AMD producing reaction will be stopped (Renton).

The objective of this research is to determine those variables most important in producing phosphatic clay slurry seals that possess low permeability. The information gained from these experiments will be used to develop field scale tests, which will in turn, be used to make recommendations for coal operators to apply phosphatic clay seals to toxic materials, thus reducing AMD.

MATERIALS AND METHODS

Samples of phosphatic clay were obtained from a phosphate mine located near Mulberry, Florida. The phosphatic clay was shipped in watertight 55-gallon containers. Samples of spoil material were obtained from an active surface mine located in central West Virginia. Both of the materials are indicative of the general physical and chemical nature of materials located in the vicinity from which they were obtained. A cover soil was also obtained from the same reclaimed area as the spoil. This cover soil will be applied over the phosphatic clay seal to prevent the subsequent drying and cracking of the seal that will occur if the seal is exposed to the atmosphere. The cover soil will also provide a vertical overburden stress or weight on the underlying seal and spoil, and it will also provide a base upon which to grow vegetation.

Several standard tests were performed on each seperate material to determine its physical characteristics. All tests were conducted in accordance with ASTM standards (ASTM, 1985) and consisted of : hygroscopic water content (D2216-80), specific gravity (D 854-83), standard proctor compaction (D 698-78), Atterberg limits (D4318-84), grain size analysis (D 422-63), and hydrometer analysis (D422-63). These tests allowed extrapolation of the results to similar materials not included in this research. Results from these tests are shown in Table 1.

The next step in the research involved developing mixing procedures for the preparation of slurries. Slurries ranging in water content from 150% to 375% by weight were prepared from the phosphatic clay. A prerequisite for acceptance of a slurry at a certain water content for futher testing was that it had the ability to be poured so that it could be applied in the field.

Before the clay was mixed with water, it was passed through a funnel with a half-inch diameter opening. Clay clods larger than this opening were broken by hand. The clay was then hand mixed with a spatula to negate any gradation that may have taken place. This procedure was followed to insure reproducible results, and to provide clay clods that could be placed in suspension by standard laboratory equipment. Initially a slow-action two-speed mixer was used to prepare the slurries. The clay however, tended to clump into large clods, and was very plastic. A rapid-action mixer, run at high speed was then used, and this produced smooth slurries. This mixer was used throughout the remainder of the research to prepare the slurries.

The major portion of the research consisted of permeating various configurations of spoil and slurry. A 10.5 cm diameter by 11.5 cm high rigid-wall double-ring permeameter (Figure 1) was used for all of the tests. The bottom of this permeameter consists of two concentric porous stones separated by a steel ring. The diameter of the ring is such that the area of the inner and outer porous stones are equal, so that under ideal conditions, the outflow is divided equally between the two porous stones. The inner ring is isolated from the sides of the permeameter, and therefore, side wall leakage, which produces inflated values for permeability, does not affect this inner stone. All values for permeability were calculated using the inflow to the permeameter. Outflows from the inner and outer stones were also recorded to make sure no side wall leakage occurred. Side wall leakage was indicated whenever the outflow from the outer stone was much greater than the outflow from the inner stone.

Distilled deionized water was used as the permeant liquid, and this was stored in a nonreactive acrylic reservoir. Pressure was supplied to the reservoir by a pressure board, which forced the water out of the reservoir into the permeameter and thereby set up a hydraulic gradient through the vertical axis of the specimen. The hydraulic. gradients used in the test ranged from 10 to 200 (cm/cm). Gradients for each test were determined solely on their ability to expedite test results.

Permeability tests were run separately on the spoil and slurry to provide a base upon which to later evaluate the effect that various combinations of spoil and slurry had on permeability. At least two permeability tests were run on specimens of each material to make sure that results were reproducible. Spoil material specimens were permeated in both the uncompacted and compacted states, and slurries ranging in water content from 150% to 375% by weight were also tested.

With the completion of these "base" permeability tests, experiments were conducted to test the permeability of layered spoil-slurry arrangements. These tests were done to determine the effects of slurry water content, slurry thickness, and degree of spoil compaction on the permeability of the layered systems. Tests were conducted using: 1) loose spoil (no compactive effort), 2) compacted spoil (100% standard Proctor), 3) high water content slurries (>275%), 4) low water content slurries (<275%), 5) thick slurries (>3cm), and 6) thin slurries (<3cm). Eight permeability tests were required to cover all possible arrangements of these variables. See Table 2 for the testing setup. Each layering arrangement was permeated for at least four pore volumes of flow. One pore volume is equal to the volume of voids in the sample. This insured complete saturation of the voids in the sample, and provided a nondimensionalized means of comparing results from different specimens. Upon completion of the test each specimen was extruded from the permeameter. Settlement of the specimen was measured, and any distinquishing features such as cracking of the slurry and rust deposition from the permeater were recorded. The specimen was then split along its vertical axis in several places, and the penetration of the slurry into the spoil was measured.

During the permeability tests, effluent from several specimens was collected for chemical analysis. This analysis included determinations of pH, alkalinity-acidity, and concentrations of iron, manganeese, aluminum, calcium, magnesium, sulfates, and phosphates. Basic elemental constituents were analyzed using atomic absorption, pH was determined using a digital ionalyzer, sulfates were analyzed using the turbidometric method, and colorimetric analysis was used to determine phosphate concentrations. These analyses were done to determine the quality of effluent produced by the spoil, and to determine what effect the addition of phosphatic clay slurry had on effluent quality.

RESULTS AND CONCLUSIONS

Typical behaviors of uncompacted and compacted spoil specimens both before and after the addition of slurry are shown in Figure 2. All of the uncompacted specimens demonstrated decreasing permeability before the addition of slurry because they were found to have settled. This impeded the flow of water, which resulted in the decreasing permeabilities. The compacted specimens exhibited steady to slightly increasing permeability before the addition of slurry because these specimens had swelled. This enabled the water to move through larger flow paths, which resulted in the increasing permeabilities. Before the addition of slurry every specimen exhibited erratic shifts in permeability between individual permeability readings. After the slurry was added an immediate decrease in permeability occurred, and the variation in permeability between individual readings stabilized somewhat. After the initial large decrease, the permeability of the uncompacted specimens tended to decrease, whereas the permeability of the compacted specimens remained the same or increased slightly.

Results from the "base" permeability tests and the eight spoil-slurry permeability tests are shown in Table 2. Before the addition of slurry, the average permeability of the uncompacted spoil was approximately 1.8×10^{-4} cm/s, and that of the compacted spoil was approximately 1.2×10^{-5} cm/s. Tests 2(1) through 2(4), performed exclusively on slurry, show it to possess an aveage permeability of approximately 3.0×10^{-6} cm/s.

Based on this last result it was expected that spoil-slurry arrangements would achieve permeabilities similar to 3.0×10^{-6} cm/s. Tests 3(1) through 6(2) show that this is not true. Permeabilities for these tests ranged from a high

Table 1. Index Properties for Spoil Material and Phosphatic Clay

Soil	Natural Water Content	Plastic Limit	Liquid Limit	Specific Gravity	Maximum Dry Unit Weight (lb/ft^3)	Optimum Water Content
Spoil	12.5	24	31	2.27	105	13
Clay	31.5	35	135	2.80	75	12

Table 2. Soil arrangement and permeability results for "base" and spoil-slurry permeability tests.

Test No.	Arrangement	Slurry Water Content (%)	Slurry Thickness (cm)	Spoil Avg. K (cm/s)	Spoil and Slurry Avg. K (cm/s)	Change in K (%)
1(1)	Loose Spoil	NA	NA	1.67x10^{-4}	NA	NA
1(2)	Loose Spoil	NA	NA	1.4 x10^{-4}	NA	NA
2(1)	Slurry	179(L)	5.56(Th)	*3.63x10^{-7}	NA	NA
2(2)	Slurry	194(L)	7.18(Th)	*1.83x10^{-6}	NA	NA
2(3)	Slurry	329(H)	2.61(T)	*4.61x10^{-6}	NA	NA
2(4)	Slurry	389(H)	4.6(Th)	*5.24x10^{-6}	NA	NA
3(1)	Compacted Spoil & Slurry	274(L)	3.10(Th)	2.09x10^{-5}	6.12x10^{-6}	70.7
3(2)	Compacted Spoil & Slurry	353(H)	3.71(Th)	2.20x10^{-5}	5.95x10^{-6}	73.0
4(1)	Loose Spoil & Slurry	174(L)	3.43(Th)	2.69x10^{-4}	2.66x10^{-5}	90.1
4(2)	Loose Spoil & Slurry	225(L)	3.93(Th)	1.53x10^{-4}	6.93x10^{-5}	54.7
5(1)	Compacted Spoil & Slurry	187(L)	1.77(T)	3.57x10^{-6}	3.93x10^{-6}	-10.1
5(2)	Compacted Spoil & Slurry	300(H)	2.54(T)	4.08x10^{-6}	3.30x10^{-6}	19.1
6(1)	Loose Spoil & Slurry	187(L)	1.27(T)	2.69x10^{-4}	9.50x10^{-6}	96.5
6(2)	Loose Spoil & Slurry	300(H)	2.11(T)	1.53x10^{-4}	2.77x10^{-5}	81.9

(H) = high water content

(L) = low water content

(Th) = thick slurry

(T) = thin slurry

K = permeability

*For tests 2(1) through 2(4) the permeability listed in column five is for the slurry.

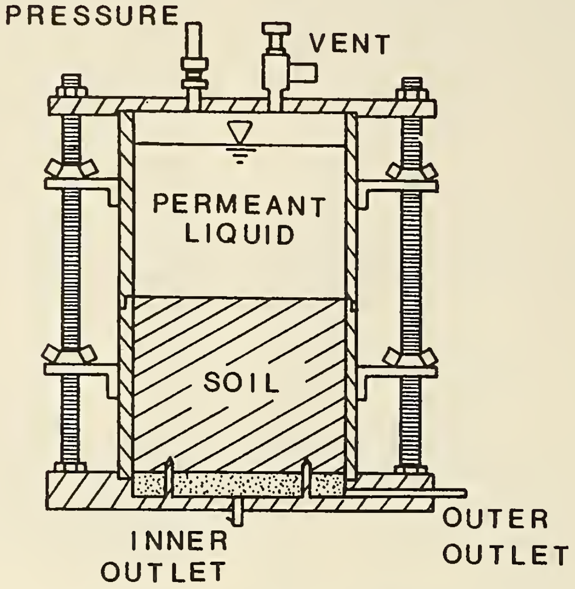
PRESSURE
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Figure 1 - Double Ring Permeameter

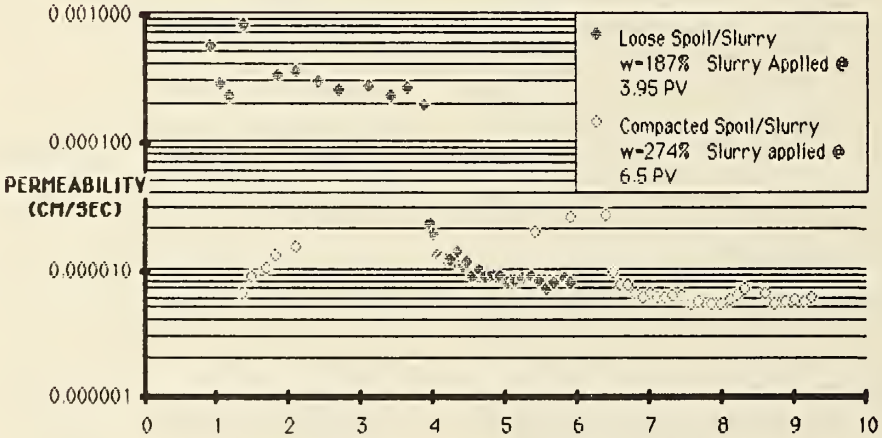

Figure 2- Typical Results From the Permeability Tests on Spoil Material and Phosphatic Slurry

of 7 x 10^{-5} cm/s to a low of 3 x 10^{-6} cm/s, with an average of 2 x 10^{-5} cm/s. All of these tests have average permeabilities higher than that of the slurry by itself. It appears from this result that the spoil plays an important part in determining the overall permeability of spoil-slurry systems. The reason for this result is not readily discernable. Variables used in tests 2(1) through 2(4), such as hydraulic gradient and slurry water content, were similar to the range of values used in tests 3(1) through 6(2). The thicknesses of the slurries used in tests 2(1) through 2(4) were approximately 2 times thicker than slurries used in tests 3(1) through 6(2). This difference however, still does not explain why the permeability of the slurry does not govern the overall permeability because test 2(3), with a thickness of 2.61 cm, has a permeability lower than six out of the eight spoil-slurry tests, which had similar slurry thicknesses.

The results in Table 2, with the exception of test 5(1), show that the addition of slurry will decrease the permeability of the spoil. The magnitude of this decrease, shown in the column labelled percent change in permeability, is not constant. On the average, a 38% decrease in permeability, with the addition of slurry, can be expected for compacted spoil, and an 81% decrease in permeability, with the addition of slurry, can be expected for loose spoil.

Table 3 lists the eight spoil-slurry specimens and their respective final permeability, percent change in permeablility with the addition of slurry, and overall performance. Each test was ranked from one to eight with respect to the final permeability, with one representing the lowest permeability, and eight representing the highest. The tests were also ranked from one to eight with respect to the change in permeability, with one representing the largest change, and eight representing the smallest. The percent change in permeability was calculated by dividing the difference between the average permeability of the spoil alone and the average permeability for the spoil-slurry system by the average permeability of the spoil alone

Table 3 demonstrates that the specimens with the lowest final permeability also tended to exhibit the smallest change in permeability when the slurry was added. Because compactive efforts in the field are often suspect, and uncompacted or undercompacted spoil may be the existing condition, it was equally important to develop spoil-slurry systems that produced low final permeabilities, and large changes in permeability with the addition of slurry. Table 3 allows for the determination of the best possible methods for applying spoil-slurry systems. By adding the point values from the final permeability column and the change in permeability column it is possible to rank the overall performance of different combinations of spoil and slurry. Lower valves of overall performance represent better systems.

From Table 3 it can also be seen that the lowest permeabilities were achieved when the spoil was compacted. The reason for this is that compaction reduces void spaces, and flow paths become smaller and more tortuous. Tests on uncompacted spoil had higher permeabilities because flow paths were not as constricted, and were straighter. As was stated previously, the permeability of the overall system is dependent on both the spoil and the slurry, and not the slurry alone. The addition of slurry can only do so much to lower the permeability of the system. The remaining decrease in permeability comes from the compactive effort applied to the spoil, with increasing effort producing lower permeability.

For the compacted specimens the water content of the slurry did not seem to have as much of an effect on the permeability as did the thickness of the slurry. This result may be misleading however, because the large range in permeabilities between the compacted specimens before the addition of slurry makes it dificult to judge the effect of slurry water content and thickness on the permeability of the compacted spoil. The overall performance ranking of the compacted specimens provided a less biased means of evaluating the effect of these variables on the permeability. Using this ranking, it appears that, in fact, the water content of the slurry was more important than the slurry thickness in determining the final permeability of the compacted spoil-slurry specimens. Higher water content slurries, whether thick or thin, produced better overall performances in the compacted specimens than did lower water content slurries. The reason for this may be that the higher water content slurries can penetrate the compacted spoil and totally or partially clog the flow paths, thereby futher hindering water movement. The lower water content slurries may not have been fluid enough to penetrate the compacted surface. Compacted specimens split after permeability testing showed no visible bulk penetration for either low or high water content slurries. The clogging of these flow spaces occurred on the microscopic level however, so blocked flow paths may not have been discernable to the naked eye.

The range in permeability between the uncompacted specimens before the addition of slurry was small, and therefore, correlation between final permeability, change in permeability, and overall performance was much better. As was the case with compacted specimens, the water content of the slurry appeared to have a greater effect on the permeability than did thickness of the slurry. In this case though, lower water content slurries produced better overall performances in the uncompacted spoil specimens. Because the uncompacted spoil had large flow paths, the higher water content slurries may have been flushed out of the specimens instead of clogging the flow paths. Lower water content slurries were less fluid, and may have provided a more stable barrier against the flow of water.

A final conclusion that can be drawn from Table 3 is that the best overall performance was produced from an uncompacted spoil specimen overlain with a low water content slurry. Attempts at compaction should still be made because compacted specimens demonstrated the lowest permeabilities, however, it is still possible to achieve satisfactory results using uncompacted spoil as long as the slurry covering the spoil has a low water content.

Results from the chemical analysis of effluent are shown in Table 4. Analyses before and after the addition of slurry were only performed on test specimens 3(1) and 3(2). The pH of the effluent for both specimens increased slightly with the addition of slurry, however, it did not reach neutrality. The reason for this result is that phosphatic clay is a relatively neutral material (pH = 7.2) so that it is difficult for it to completely buffer an acidic material.

The affinity of phosphate ions for metal ions is dramatically demonstrated in the large reductions in the concentrations of iron, manganeese, magnesium, and aluminum, with the addition of slurry. The absence of any detectable concentration of phosphate ions after the addition of slurry shows that the phosphate ions were completely consumed in various chemical reactions with the metal ions to produce insoluble metal phosphates. A visual inspection of the color of the effluent also indicated that the phosphate ions were effective in removing the metals. The yellow color of the effluent, common in AMD, was apparent before the addition of slurry, however, with the addition of slurry the effluent became clear within one pore volume of flow.

The increase in the concentration of calcium with the addition of slurry is due to the dissolution of the calcium phosphate contained in the phosphatic clay. This result leads to an increase in the hardness of the effluent, however, this consequence must be weighed against the advantages of the large removal of heavy metals.

Sulfate concentrations were also reduced, but the final concentrations were still high. The reductions in sulfate concentration of the two specimens are reflected in the increase of pH for both specimens.

A discrepency in the iron concentration existed for test specimen 3(2). The initial concentration was very low, but increased significantly with the addition of slurry. An explanation for the initially low concentration may be that the sample of spoil used to prepare the specimen did not contain a representative amount of pyrite. The increase in iron concentration after the addition of slurry may be due to outside sources of iron that were introduced to the specimen during testing. An inspection of the permeameter after the permeability test was completed indicated that spalling of the interior wall had occurred. This could have provided a large amount of iron that flowed down the interface between the permeameter and the specimen.

In conclusion, it appears that the compactive effort applied to the spoil is the dominant variable in determining the permeability of spoil-slurry systems. Larger compactive efforts result in lower permeabilities. Slurry water contents are also important in determining the permeability of spoil-slurry systems. Low water content slurries ranging from 150% to 250% by weight should be applied to uncompacted spoils, and high water content slurries ranging from 250% to 350% by weight should be applied to compacted spoils. The thickness of the slurry does not seem to be important in determining the permeability of the spoil-slurry system. It may be advantageous, however, to use thick slurries to better insure that any cracks that may develop in the seal do not pass completely through the seal. Before the addition of slurry, uncompacted spoil material has an average permeability of 1.8 x 10^{-4} cm/s. After the slurry has been applied the average permeability can be expected to drop to 3.3 x 10^{-5} cm/s. Before the addition of slurry, compacted spoil material has an average permeability of 1.3 x 10^{-5} cm/s. After the slurry has been applied the average permeability can be expected to drop to 4.8 x 10^{-6} cm/s. Spoil material should be compacted before the application of slurry. Relatively low permeabilities can still be produced in uncompacted spoil if the slurry water content is kept low. The addition of slurry also greatly reduces the concentrations of iron, manganeese, magnesium, aluminum, and sulfates in the effluent through the formation of insoluble metal phosphates. The concentration of calcium in the effluent will increase due to the dissolution of calcium phosphate in the slurry. All of the various chemical reactions will result in a slight increase in the pH of the effluent with the addition slurry.

Results from these tests will be applied to field tests during the summer and fall of 1988. It is hoped that these test will futher enable the authors to define the optimum spoil-slurry system, and allow them to develop procedures for applying this technology to the coal mining industry.

ACKNOWLEDGEMENTS

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Table 3. Ranking of spoil-slurry tests for the lowest final permeability, greatest change in permeability, and best overall performance, based on results from Table 1

Test No.	Soil Arrangement	Final Permeability(1)	Change in Permeability(2)	Sum of Columns 3 and 4	Overall Performance(4)
3(1)	Compacted Spoil & Slurry	4	5	9	4
3(2)	Compacted Spoil & Slurry	3	4	7	2
4(1)	Loose Spoil & Slurry	6	2	8	3
4(2)	Loose Spoil & Slurry	8	6	14	6
5(1)	Compacted Spoil & Slurry	2	8	10	5
5(2)	Compacted Spoil & Slurry	1	7	8	3
6(1)	Loose Spoil & Slurry	5	1	6	1
6(2)	Loose Spoil & Slurry	7	3	10	5

(1) 1 = lowest final permeability 8 = highest final permeability
(2) 1 = largest change 8 = smallest change
(3) Numbers determined by adding the final permeability ranking to the change in permeability ranking
(4) Overall performance determined by ranking numbers in column five from lowest to highest, with lowest being the best.

Table 4. Results of Effluent Analysis Before and After the Addition of Phosphate Clay Slurry

Test		pH	Fe	Mn	Ca	Mg	Al	SO_4^{-2}	PO_4^{-3}
3(1)	Before Slurry	3.89	81.9	248	249	557	623	9320	0.25
	After Slurry	5.73	5.6	17	658	80	6	2145	--
3(2)	Before Slurry	4.14	13	271	300	586	345	8580	0.25
	After Slurry	4.64	160	107	603	78	13	2040	--

Concentrations are in parts per million

LABORATORY AND FIELD TESTING OF A SALT-SUPPLEMENTED CLAY CAP AS AN IMPERMEABLE SEAL OVER PYRITIC SLATES[1]

Eric W. Murray, S. Paul Goudey, Ron G. L. McCready and Joe Salley[2]

Abstract -- During construction of a taxiway at Halifax International Airport in Nova Scotia in 1982, about 225,000 cubic metres of fractured waste pyritic slate material was disposed in a pile covering about 7 hectares on the airport property. As a result of air and water infiltration and the presence of Thiobacillus ferrooxidans, this waste rock pile has been seeping a heavy metal laden acidic effluent similar to acid mine drainage. Because sufficient quantities of a relatively impermeable clay overburden were present on site, it was decided to apply a compacted clay cap to the pile to reduce air and water infiltration. From previous experience it was known that concentrations of greater than 1% sodium chloride in the aqueous phase are inhibitory to Thiobacillus ferrooxidans. Laboratory studies confirmed that addition of a layer of highway salt beneath the clay not only inhibits the production of acid drainage, but also enhances the sealing capacity of the clay. Placement of the salt supplemented clay cap was undertaken in 1986 and 1987. Early observations indicate a reduction in the volume and an improvement in the quality of water seeping from the waste rock pile.

INTRODUCTION

Halifax International Airport in Nova Scotia, Canada is located on a band of highly mineralized pyritic slate bedrock. As part of construction of an aircraft taxiway in 1982, a mass of this slate was blasted and excavated. About 225,000 cubic metres of waste slate material was deposited in a pile covering about 7 hectares adjacent to the taxiway. Several months after the start of construction an effluent of acid water laden with heavy metals began seeping from the waste rock pile and from the subdrains beneath the taxiway. At the direction of regulatory authorities, a system was immediately constructed to collect this acid drainage and to treat it by addition of hydrated lime. At the time, it was thought that the acid drainage would subside in several months.

When the acid seepage continued, unabated, for five years, a decision was made to place an impermeable seal over the entire pile to restrict oxygen and water penetration into the fractured pyritic slate. As sufficient quantities of a relatively impermeable clay were present adjacent to the pile, a compacted clay cap was chosen as the seal. Because Transport Canada had little experience in the mitigation of acidic drainage, an interdepartmental committee was struck to advise on the "state-of-the-art" technology in this area. The Committee charged the Canada Centre for Mineral and Energy Technology (CANMET) to investigate the feasibility of incorporating a salt layer between the pyritic slate waste and the overlying clay cap in order to reduce acid formation through bacteriostatic activity as well as through the oxygen depletion achieved by the clay capping. This paper describes the laboratory study that tested this hypothesis, the application of the salt-supplemented clay cap in the field and early indications of the effects of the capping on acid drainage from the waste rock pile.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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MATERIALS AND METHODS

Laboratory

Two laboratory studies were conducted to determine: (1) the effect of road salt on the production of ferric iron in a column and (2) the effectiveness of a combination salt/clay cap on the percolation rate. These studies were, in part, an outgrowth of past work on the reclamation of solonetzic (sodic clay-pan) soils, where it was observed that Thiobacilli were unable to sustain viable populations in soils containing 4.8 meq of Na^+/100 g of soil (McCready 1982, McCready and Krouse 1982). Later studies on the adaptation of Thiobacilli to growth in saline waters indicated that T. ferrooxidans could not tolerate sodium chloride concentrations greater than 1% weight/volume. Thus, this laboratory study was conducted to test the hypothesis that the incorporation of a salt layer between the pyritic slate waste and the overlaying clay cap would provide bacteriostatic activity to reduce the formation of acid in addition to the oxygen depletion effect of the clay capping.

Samples of Halifax slate and clay overburden from the Halifax Airport were provided to CANMET to carry out the laboratory study. The Halifax slate is comprised mainly of slate and metagreywacke with minor quartzite. It is rich in sulphides, with pyrite and arsenopyrite and minor amounts of pyrrhotite, sphalerite and chalcopyrite. Whole rock laboratory analyses reveal metal contents in the ranges indicated in table 1. (Lund 1987.)

A summary of the grain size analysis of four samples of the clay overburden is found in table 2.

A hydrometer analysis on sample 4 revealed that 34% of the weight of the sample is clay size particles (0.005 mm grain size or smaller). This overburden is described by the Unified Soil Classification System (U.S.C.S.) as Silty, Sandy Clay and Sandy, Silty Clay. (CL). Its permeability is 4 X 10^{-7} cm/sec.

Table 1 -- Metals found in Halifax slates.

Element	Percentage	ppm
Aluminum	9-13	
Iron	3-6	
Manganese	0.01-0.04	
Cobalt		10-80
Nickel		40-270
Lead		10-48
Arsenic		4-19
Copper		18-46
Zinc		70-210

Table 2 -- Clay overburden - percent passing standard sieves (by weight).

Sample	19 mm	9.5 mm	4.75 mm	425 micrometer	75 micrometer
1	100	100	97	87	63
2	100	99	96	82	53
3	100	100	99	86	60
4	100	99	98	87	65

Effect of road salt on ferric iron production

For the first laboratory study four columns (6 cm in diameter and 50 cm in length) were loaded with one kg of Halifax slate and overburden as shown in Fig. 1. In two of the four columns, 5 grams (less than 10 mm thickness) of road salt (NaCl) was placed on the surface of the slate. One salt-supplemented column and one unsupplemented slate column were inoculated with 500 mL of a 96-hour culture T. ferrooxidans grown on the low phosphate medium (McCready et al. 1986). The other salt-supplemented column and the remaining unsupplemented column were trickle leached with distilled water. The distilled water and the T. ferrooxidans cultures were circulated through the columns using a Gilson Minipuls-2 peristaltic pump at a flow rate of 300 mL/h. Samples of the recirculating solutions were collected periodically from the two columns for pH determinations and ferric iron analyses. The total volume of solution for each column was kept constant at 500 mL by the periodic addition of distilled water.

Effect of a salt and clay capping

In the second laboratory study, which assessed the effect of a salt (NaCl) and clay cap, two additional columns were prepared as shown in fig. 2. The test column had a layer of road salt placed between the pyritic slate sample and the clay layer which was tightly compacted in both columns. Two hundred and fifty mL of distilled water was added to each column to assess the percolation rate through the clay.

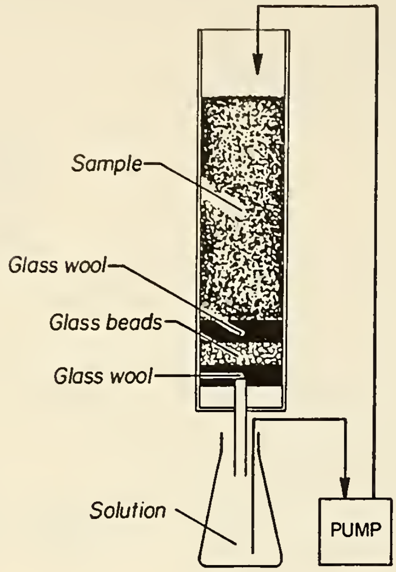


Figure 1. -- Column design for testing the effect of 1.5% NaCl in solution.

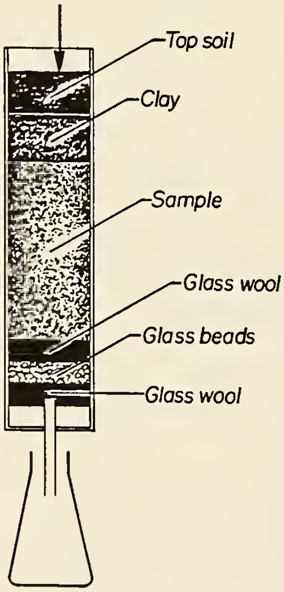


Figure 2. -- Column design for testing clay-capping.

Field

Field testing of the salt-supplemented clay cap was carried out on the pyritic slate waste rock pile at Halifax International Airport, which, being constructed on a slope, ranged in depth from about 2 m to 10 m. The waste slate was surrounded on three sides by clay berms and was covered by a loose clay layer varying in thickness from 100 mm to 500 mm. The top of the pile, although generally flat, had several depressions allowing water to pond. Side slopes varied from 2.5:1 to 4:1, which had led to significant erosion of the clay slope cover. The acid drainage collection pond is located at the base of the slope on the west side of the pile (fig. 3).

The field work described here resulted from a contract awarded in October 1986 to construct surface drainage intercept channels at the base of the north, east and south sides of the waste rock pile; reshape the top surface of the pile to provide a uniform gradient of 1.5%; supply highway coarse salt over the entire surface of the pile (including side slopes) at the rate of 11.5 kg/m^2; place a compacted clay cover 750 mm thick over the entire area; supply and place 150 mm topsoil over this; place sod on the side slopes and areas of higher water flow on top; and hydraulically seed the remainder of the site. Fig. 4 is a typical section through the finished work.

Work commenced immediately and by December 1986, when work stopped due to winter conditions, the top of the pile had been regraded, the coarse salt had been applied, and a 375-mm thick compacted clay layer had been installed over the entire top surface. The surface water intercept channels were constructed in March 1987. Due to the low permeability and resulting high water retention of the salt-supplemented clay layer, work was unable to start again until July 1987. The final 375-mm compacted clay layer was completed by early September, and the 150 mm of topsoil was placed by the end of September. Sodding was completed by October 15, 1986, but the hydraulic seeding remains to be done.

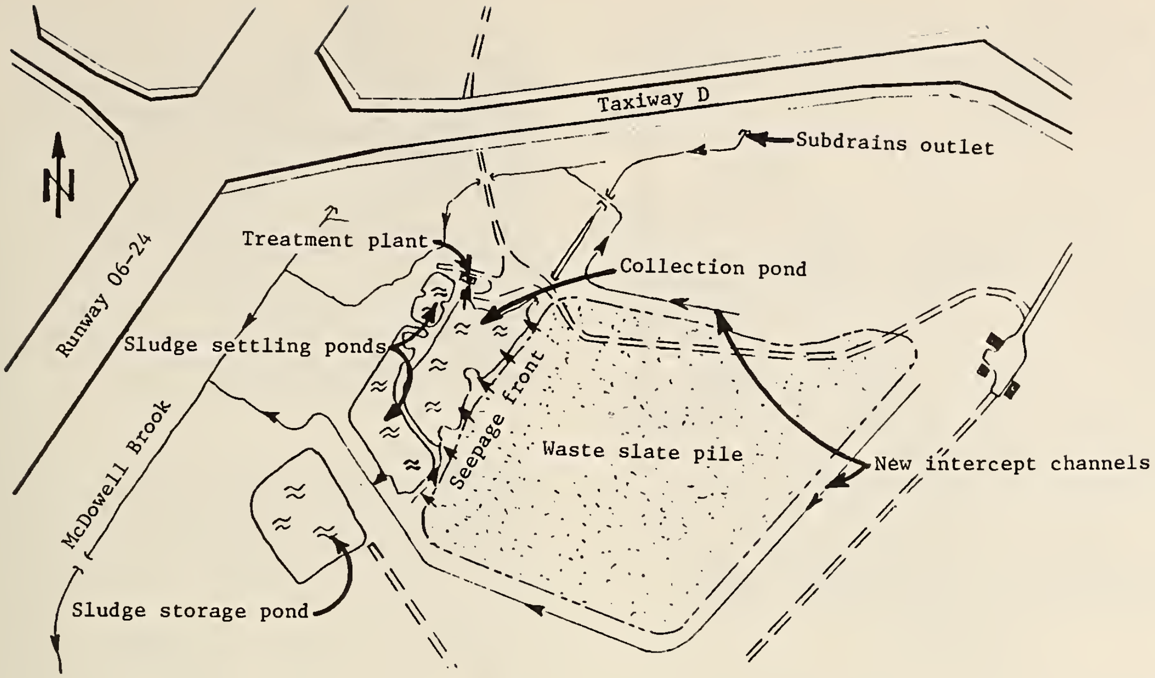

Taxiway D
Subdrains outlet
N
Runway 06-24
Treatment plant
Collection pond
Sludge settling ponds
Seepage front
Waste slate pile
New intercept channels
McDowell Brook
Sludge storage pond

Figure 3. -- Site plan.

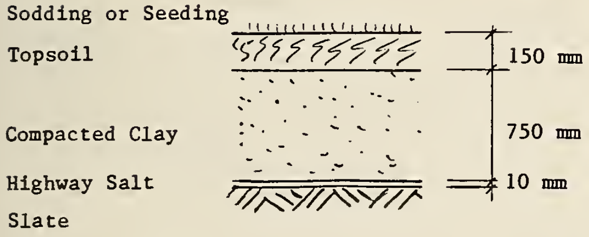

Sodding or Seeding
Topsoil
Compacted Clay
Highway Salt
Slate
150 mm
750 mm
10 mm

Figure 4. -- Typical section through finished work.

RESULTS AND DISCUSSION

Laboratory

Effect of road salt on ferric iron production

When the cultures of T. ferrooxidans were recirculated through the pyritic slate columns the soluble ferric iron content of the solution decreased due to adsorption of the iron to the clays in the slate/overburden mixture. After one month, the soluble ferric iron concentration of the leachate increased in the non salted column due to microbial activity (fig. 5). This was confirmed by microscopic examination of the leachate; after 50 days the leachate contained about 10^6 organisms/mL.

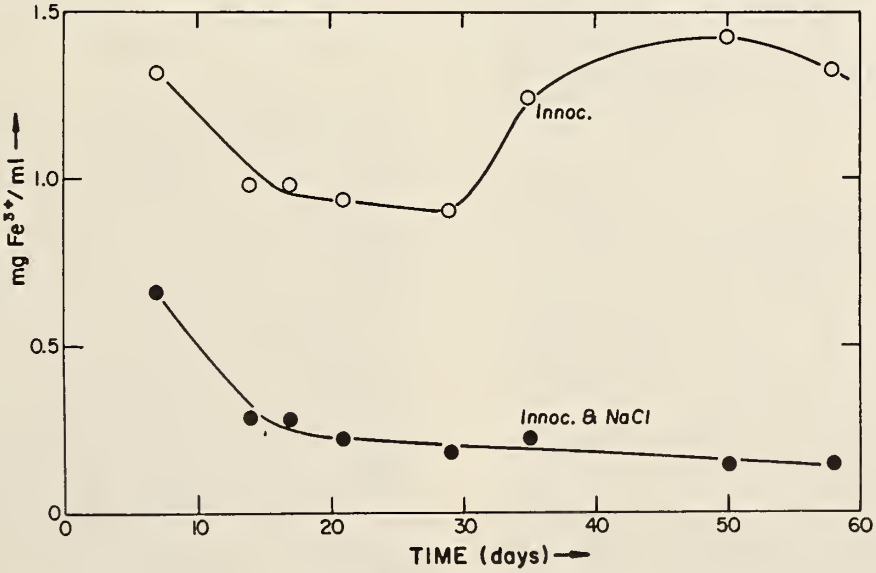


Figure 5. -- Fe^{+3} in test column effluents.

In contrast, in the salt-treated columns, the soluble ferric iron content decreased over the first 20 days and remained at a minimal concentration until the experiment was terminated. No active bacterial cells were observed during microscopic examination of the leachate.

In the two columns leached with distilled water there was very little iron release and no T. ferrooxidans could be detected in the leachate. Extensive physical breakdown of clay components of the overburden was observed in the salt-supplemented column. The continuous recycle of the saline solution most likely resulted in the stripping of calcium ions from the clays and the sodium ion replaced the calcium in the cation exchange sites. This resulted in the formation of clay fines which plugged the column after 35 days. Repeated back-flushing of the column finally resulted in clearing of the clay fines and the experiment was continued to the 58th day.

Effect of a salt and clay capping

After compacting the clay and soil layers on the two columns, 250 mL of distilled water was placed on the top of the columns. None of this water penetrated through the clay layer in either column. After two weeks the added water had evaporated and the soil and clay layers were allowed to dry out.

The clay layer in the column without salt cracked vertically and on rewetting with 250 mL of water, the water penetrated through the clay layer and the column within 4 hours; the clay seal has not resealed to date. In contrast, the clay and salt seal in the other column cracked horizontally on drying. When 250 mL of water was reintroduced it took 12 hours for the water to penetrate through the clay and column. An addition of a second 250-mL aliquot of water, the clay resealed itself and no additional water percolation through the column has been observed to date.

The water which passed through these two columns initially was analyzed for iron content and pH. These values are presented in table 3.

Table 3 -- pH and ferric iron concentration of the initial effluent and after 250 mL of effluent had passed through the clay sealed columns.

Seal	Effluent	pH	Fe^{+3} ppm
Clay alone	First 5 mL	2.47	292
	After 250 mL	2.60	82
Clay + NaCl	First 5 mL	2.41	98
	After 250 mL	2.51	34

As stated above, the clay-capped column without salt has not resealed to date. After drying and cracking, with subsequent resettling of the clay, water percolation was observed to be 55 mL/day. After four months, the percolation rate has declined to 22 mL/day, and there has been 0.75 increase in the effluent pH over this period (fig. 6). In contrast, the column with salt added sealed completely after drying and the subsequent addition of 500 mL of water; to date no further effluent has been collected. Removal of an interstititial water sample indicated that the water had a pH of 2.98 with a very low iron content (48 ppm).

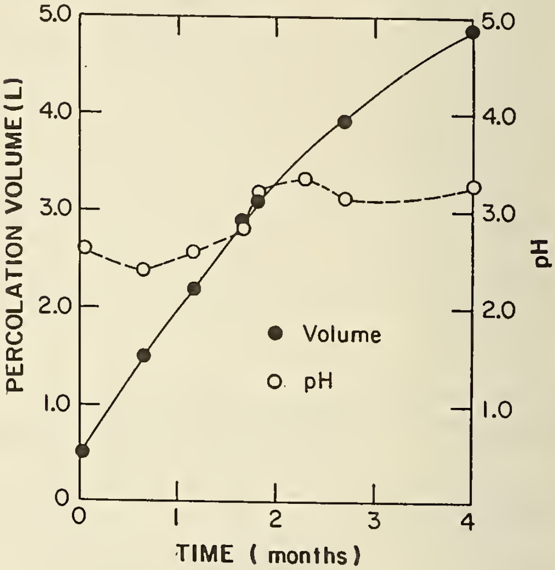
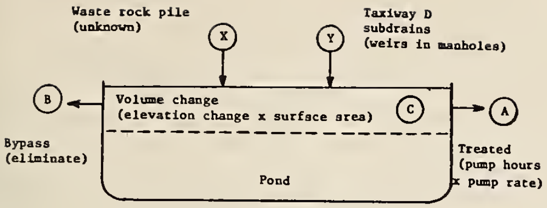


Figure 6. -- Volume and pH of the effluent from the clay-capped column without the salt layer

Field

As indicated in figure 3, all seepage from the waste rock pile and from the pavement subdrains beneath Taxiway D is collected jointly in the treatment plant collection pond west of the waste rock pile. The taxiway subdrain flows are directed to this pond by a single channel. Because flows from the waste rock pile enter the collection pond along a seepage front, there are no specific quality nor quantity data available for this seepage. The quantity of seepage from the waste rock pile must therefore be calculated by subtracting the known taxiway subdrain flow volume from the known volume pumped through the treatment plant, while adjusting for changes in the level of the collection pond (fig. 7). The quality of the water at the plant intake represents a combination of the quality of water from the subdrains and from the waste rock pile.


Waste rock pile (unknown)
X
Y
Taxiway D subdrains (weirs in manholes)
B
Volume change (elevation change x surface area)
C
A
Bypass (eliminate)
Treated (pump hours x pump rate)
Pond

$$X + Y = A + B \pm C$$

$$X = A + B \pm C - Y$$

Figure 7. -- Method of calculating seepage volume.

Figures 8, 9, and 10 plot the concentrations of acidity, iron, and aluminum in seep water at the outlet of the Taxiway D subdrains and at the inlet to the treatment plant, beginning 10 months prior to start of improvements and continuing to present.

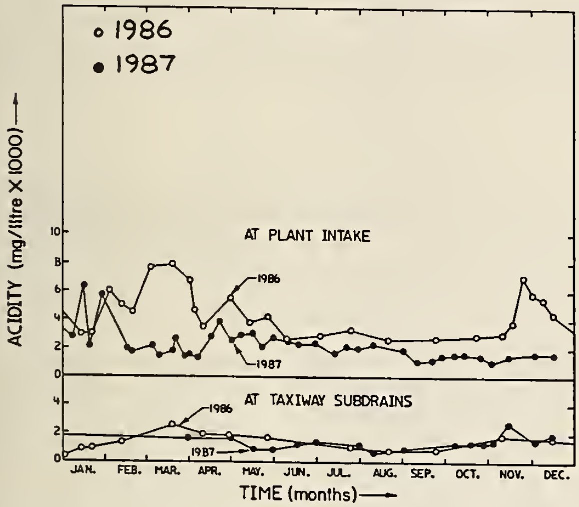


Figure 8. -- Concentration of acidity in seep water.

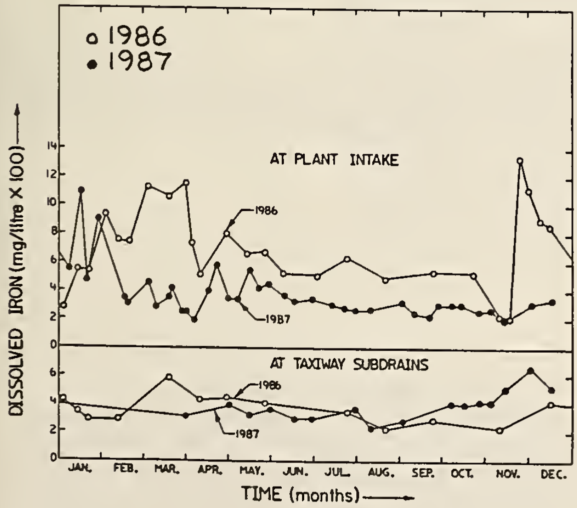


Figure 9. -- Concentration of iron in seep water.

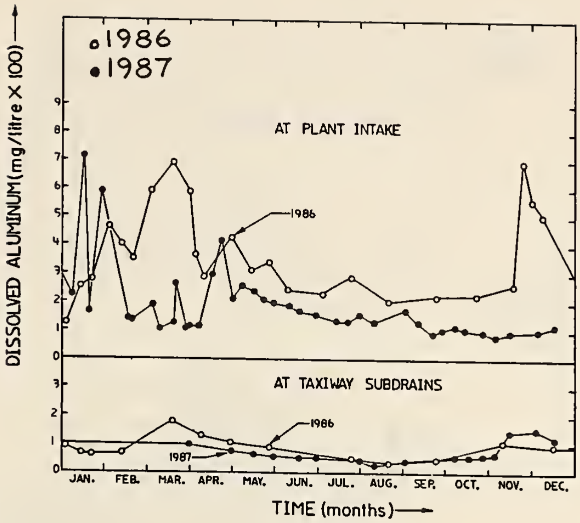


Figure 10. -- Concentration of aluminum in seep water.

All three parameters exhibit the same trend. During initial reshaping of the waste rock pile in November, 1986, a large rainfall on areas of freshly exposed pyritic slate caused concentrations of acidity, iron, and aluminum at the plant intake to jump to levels as high as or higher than previously recorded at this station. These increased concentrations did not diminish to pre-construction levels until mid-February of 1987, about three months later. With the salt layer and half the thickness of the clay cap in place, the 1987 spring runoff resulted in much lower concentrations of the three parameters at the plant intake than for the previous year. Since that time all parameters at this station have been at concentrations 6% to 35% lower than the same period of the previous year. Because the concentrations of these parameters have at the same time remained relatively constant at the outlet of the taxiway subdrains, the improvement in the quality of water seeping from the waste rock pile has been even more pronounced.

Because of variations in amounts of precipitation among seasons and from year to year, the discharge volume/unit of rainfall during the same time period was used to determine the impact of the salt supplemented clay cap on the volumes of water seeping from the waste rock pile. The total volume of seep water was calculated per Figure 6 and then divided by the total rainfall during the same time period to yield the unit discharge volume. Figure 11 shows this unit discharge for specific rainfall events for which all necessary data are available, beginning in August 1986 (when an hour meter was first installed on the pump at the treatment plant) and continuing to present. Figure 11 also illustrates the monthly average unit discharge volumes from the waste rock pile over the same time span.

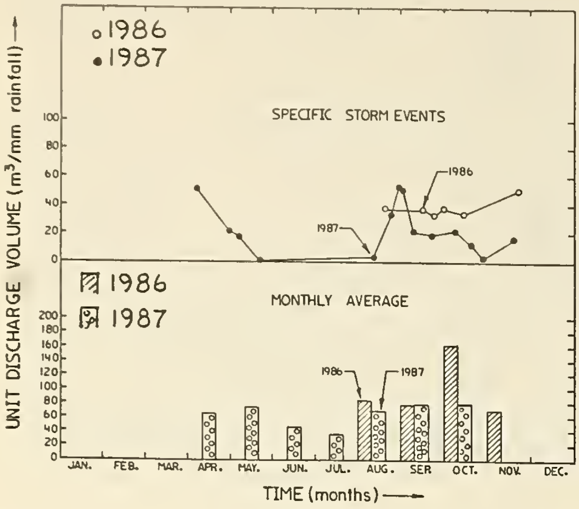


Figure 11. -- Waste rock pile unit discharge quantities.

Prior to start of construction of the cap, the unit discharge volumes over a 24-hour period for five specific rainfall events for which data are available lay consistently between 33 and 40 m^3 of discharge/mm of rainfall. The storm during November 1986, on the freshly regraded waste rock pile resulted in a unit discharge volume from the pile of over 50 m^3/mm.

Because of winter conditions, no more data are available until the end of April 1987, at which time the salt layer and half the thickness of the clay cap had been installed. Unit discharge volumes for four specific storms varied from about 20 m^3/mm at this time to near zero in mid-August (when the clay cap was nearly completed). During three storms during late August and early September, after one of the driest summers on record, the unit discharge volume rose inexplicably to 35 and then to over 50 m^3/mm. In six storms since this, the yield dropped to about 20 m^3/mm or less.

The monthly average unit discharge volumes have trended downward from a high of 160 in October 1986 (just prior to start of improvements) to less than 40 in July of 1987. Again, August of 1987 has an unexplainably higher yield, although it is still lower than August of 1986. This yield held approximately constant through September and October, 1987.

Conclusions

In the laboratory study, preliminary work confirmed that road salt inhibited the production of ferric iron. In further work, the addition of a salt layer between the pyritic slate and the clay cap resulted in a higher water retention time by the clay cap as indicated by the longer time required for drying and cracking of the clay layer. On drying, the clay cap cracked horizontally, rather than vertically, thereby preventing oxygen penetration to the underlaying slate. On rewetting, the salt induced swelling of the clay results in the reformation of an impermeable seal more quickly than in the absence of salt. In addition, if the clay should rupture, any water percolation would result in the leaching of soluble salt into the slate, thereby inhibiting any Thiobacilli within the water-penetrated slate.

The salt-supplemented clay cover installed in the field on the waste rock disposal site has caused an initial decrease in levels of acidity and dissolved iron and aluminum in the water seeping from the pile and a gradual decrease in the volume of seepage from the pile. After one winter with only one half of the thickness of the clay in place, the effectiveness of the cap has not diminished. Monitoring is being continued to determine the long term effectiveness of this sealing method.

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McCready, R. G. L. and H. R. Krouse 1982. Sulfur isotope fractionation during the oxidation of elemental sulfur by Thiobacilli in a Solonetzic soil. Can J. Soil Sci. 62: 105-110.

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THE PARTITIONING OF FLOW COMPONENTS OF ACIDIC SEEPS FROM SURFACE COAL MINES AND THE IDENTIFICATION OF ACID-PRODUCING HORIZONS WITHIN THE BACKFILL[1]

Daniel T. Snyder and Frank T. Caruccio[2]

Abstract.--Two surface coal mine backfills in Upshur County, W.V. were monitored for 3 years to determine the relationship between the hydrology and the mine drainage quality. The recharge of the ground water system was determined by analyzing the response of the water table to precipitation events. Recharge occurs in two ways either by rapid recharge by runoff draining into highly permeable randomly oriented channels during times of high intensity - short duration rain events or regional downward migrating wetting fronts occurring during low intensity - long duration rains and spring thawing events. In the former case,water movement through the unsaturated zone was found to be from 12 to 30 ft/day. Seep flow is comprised of shallow subsurface lateral flow (interflow) and deep ground water discharge (baseflow). Using regression analyses, water table elevations were correlated with baseflow and subsequently used to estimate the baseflow component of the total flow of the acidic seeps. Accordingly, total flow minus baseflow represents the interflow component of the seep. With these flow relationships, variations in seep chemistry were correlated with various flow components to identify the sources of acidity within the backfill. At one mine, interflow did not correlate with acid concentration, whereas at the second mine, interflow was negatively correlated with acidity. Therefore, runoff draining into the permeable channels of the vadose zone, flowing as interflow in the backfill, does not appear to be a major acid contributor. Instead most of the acidity is produced by low-intensity long-duration generated wetting fronts (spring recharge events), infiltrating the system at field capacity. This creates a reservoir of acidic water that sustains the acid mine drainage seeps for the remainder of the water year.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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INTRODUCTION

Water is a crucial factor in the production of acid mine drainage, not only in the oxidation of pyrite but as a medium to transport the reaction products, including acidity and sulfate, to a discharge point. Previous studies of the relationship between ground water flow in backfills and acid mine drainage quality include Collier et al. (1970), Oertel and Hood (1983), Ladwig and Campion (1985), Lusardi and Erickson (1985), and Erickson and Ladwig (1986). The current study differs from the above studies in that it was designed to delineate the interflow and baseflow contributions to seep discharge, determine the relationship between the location of the flow path in the backfill and the resultant seep quality, and identify the acid-producing horizons within the backfill. This information can provide the basis for the design and development of in-situ acid mine drainage abatement strategies.

METHODOLOGY

Data Collection

Two reclaimed surface coal mines in Upshur County, W.V. were selected for detailed hydrogeochemical analysis (fig. 1). The Eight Acre site is a small, unlined, northwestern portion of a larger 15 ha refuse pile which has been almost completely covered with a 20 mil PVC plastic liner. A high-volume acidic seep emerges from the northwestern toe of the Eight Acre site. The Forty Acre Well site is a northwest-southeast oriented strip bounded to the north by a highwall. Acidic drainages are found at the western edge of this site.

Beginning in the spring of 1985, alkaline recharge trenches were installed on the Forty Acre Well site to mitigate acid seeps through alkalinity additions (Caruccio, et al., 1984). Treatments were through the construction of permeable trenches that contained sodium carbonate briquettes and crushed limestone (designed to intercept and divert chemically modified surface runoff into the backfill), and covering the surface of the mine with a veneer of crushed limestone.

Thirteen observation wells were installed on the two sites between 1983 and 1985 (10 on the Forty Acre site and 3 on the Eight Acre site). The 4 and 6-inch (10-and 15-cm) diameter cased (but not grouted) wells fully penetrate the spoil and are screened along a 10 ft (3-m) interval at the bottom of the wells. Water levels in these wells were measured on a weekly basis at the Forty Acre well site and daily at the Eight Acre site.

During the time frame of this study seep discharge was measured daily at seeps 6 and 7A which emanate from the Eight Acre site and the Forty Acre Well site, respectively. Flows are routed through 1-foot long, 8-inch-diameter, PVC pipes located as close to the seeps as possible. Discharge is measured using an 8-inch-(20-cm) diameter V-notch weir.

Precipitation has been monitored on a daily basis at the site since 1981, using a 4-inch (10-cm) diameter all-weather rain gauge.

Water samples have been collected from seeps 6 and 7A on a weekly basis since 1983 and 1985, respectively. These samples are analyzed for temperature, pH, specific conductance, acidity, alkalinity, and sulfate at the Environmental Hydrogeology Laboratory at the University of South Carolina.

Data Analysis

Seep flow is comprised of shallow subsurface flow (interflow) and deep subsurface flow (baseflow). Interflow is further defined as the ground water flow that occurs in the unsaturated zone, while baseflow is the ground water flowing in the saturated zone below the water table.

To separate the total seep flow into its constituent components of baseflow and interflow, it was necessary to predict the baseflow components of the total flow. Using Darcy's law and relating the seep discharge to a function of the head, the baseflow component of the total seep discharge is directly proportional to the water table elevation measured in a well.

At the Eight Acre site, the partitioning of seep 6 into its flow components was accomplished through multiple linear regression, to examine the relationship between the discharge of seep 6 (during periods of little or no interflow input) and the water table elevation, as measured in wells 6, 6A, and 6B.

During the calibration of the regression model, discrete sets of observations were used to remove the influence that interflow might exert on the seep flow. Seep flow data were discarded if they were measured within 6 days of a precipitation event of 0.25 inch (0.64 cm) or greater. Additionally, because snowmelt might contribute interflow for a much longer period after the precipitation occurred, all observations were discarded when 2 inches (5 cm) or more of snow was on the ground.

Once calibrated, the regression model can be used to predict the baseflow discharge by substituting the estimated regression coefficients and intercept (as determined during the calibration process) and using the water table elevations measured in the wells.

The seep flow from the Forty Acre Well site was analyzed in a fashion

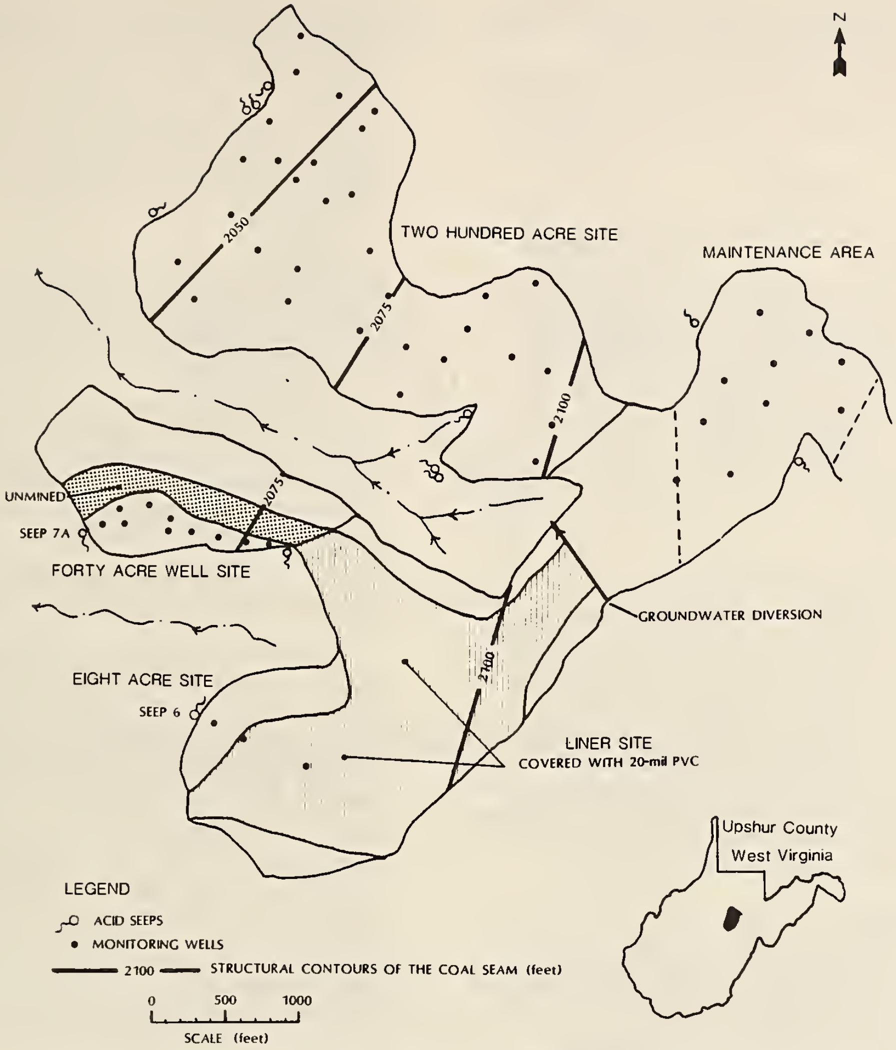
N
TWO HUNDRED ACRE SITE
MAINTENANCE AREA
2050
2075
2100
UNMINED
SEEP 7A
2075
FORTY ACRE WELL SITE
GROUNDWATER DIVERSION
2100
EIGHT ACRE SITE
SEEP 6
LINER SITE
COVERED WITH 20-mil PVC
Upshur County
West Virginia
LEGEND
ACID SEEPS
MONITORING WELLS
2100 STRUCTURAL CONTOURS OF THE COAL SEAM (feet)
0
500
1000
SCALE (feet)

Figure 1. Map of mine sites used in this study and their location.

similar to that used for the Eight Acre site. Because the water levels in the wells at the Forty Acre Site are highly correlated with each other (see fig. 2), a single well was selected for use in the regression analysis of water elevation and seep discharge. Well 14 was selected because it had the highest r-square (r^2) value of any well when used as the regressor variable.

Seep flow and water level observations used to calibrate the Forty Acre Well site regression model were selected using the same criteria as those used for the Eight Acre Site.

Once the baseflow contribution to the total seep flow has been determined, and assuming that other contributions to seep flow, specifically overland flow and direct input from precipitation, are negligible, subtracting the predicted baseflow from the observed total seep flow yields the interflow.

Having separated seep flow into its baseflow and interflow components, seep chemistry can now be correlated with the magnitude of each flow component to determine sources of acidity in the backfill. However, an important consideration should be recognized in this type of analysis. The total flow of the seep is an aggregate of ground water flow components whose origins are spatially and temporally distributed throughout the backfill. Correlation normally only evaluates the relationship between two variables without regard for temporal separation. While the effects of some variables are immediate, such as the transfer of the pressure head through the saturated zone due to a change in the elevation of the water table, the effects of other variables are delayed, such as the mass transfer of ground water from its place of infiltration through the minespoil to the seep. A time series analysis called cross-correlation, which creates a series of correlations comparing the effect of one variable with the delayed impact on another variable (the unit of delay time is called the lag or lag time), was used to circumvent this problem. Correlations are conventionally calculated from 0 to n/4 lags, where n is the total number of lags in the time series (Davis 1986).

RESULTS

Water Table Response to Precipitation

By comparing the well hydrographs with the precipitation data, the response time between a precipitation event and water table recharge in the vicinity of a well can be established. In addition, due to the excellent data coverage for the wells at the Eight Acre site, cross-correlation can be used to determine the response time between precipitation and changes in water level elevations.

The hydrograph of well 6 (fig. 3) shows the water table responding to precipitation events of about 1 inch or greater with a moderate increase in water elevation. Cross-correlation analysis indicates that well 6 responds in as little as 1 day and as long as 5 days, with a mean of 2 days. The unsaturated thickness of the spoil at well 6 is approximately 60 ft (18 m). Therefore, the water that recharges the water table moves with an average downward velocity of 30 ft/day (9 m/day) through the backfill.

The hydrograph of well 6A (fig. 3) reveals a dramatic change in the response character of the well which occurred around March 1985, at which time post-holes spiked with caustic soda (NaOH) were constructed at the Eight Acre site to intercept flow channels, that feed Seep 6A. Prior to March 1985, well 6A responded to precipitation in a manner similar to that of well 6 though with a slightly greater intensity and a faster response time. After March 1985 well 6A exhibited a flashy character, responding immediately and strongly to precipitation events of 1 inch (2.5 cm) or greater. Statistical analysis indicates that well 6A has a minimum response time of less than 1 day and a maximum response time of 1 day with a mean of less than 0.5 day. The unsaturated thickness of the spoil at well 6A is about 15 ft (4.6 m). Water recharging this area has an average downward velocity of greater than 30 ft/day (9 m/day) through the backfill.

The results from cross-correlation analysis of precipitation and the water elevation in well 6B show a consistent response time of 5 days. The mine-spoil unsaturated thickness at well 6B is approximately 90 ft (27 m). If water is recharging vertically through the backfill in the vicinity of well 6B, then it has a downward velocity of 18 ft/day (5.5 m/day). However, the mine-spoil around well 6B is at the edge of a plastic liner installed to inhibit infiltration. There are several possible causes for the change in the water table as observed at well 6B: 1) the liner may be leaking, 2) channelized flow paths may direct the water laterally through the unsaturated zone from the unlined portions of the mine, 3) ground water may be moving through the saturated zone downslope (with respect to the mine-floor) or a combination of (2) and (3).

At the Forty Acre Well site all wells display similar responses to precipitation events, albeit with varying magnitudes (fig. 2). Response times appear to be on the order of a few days.

Collier et al. (1970) have also observed well responses to precipitation events within 24 hours at a mine-spoil in Beaver Creek Basin, KY indicating that recharge is capable of moving rapidly through the unsaturated zone.

Relationship Between Baseflow and Water Table

Using regression analysis, a strong predictive relationship (adjusted r^2 = 0.89 and a p-value (or probability) = 0.001) was established between baseflow and water levels in the observation wells at the Eight Acre site. The baseflow hydrograph predicted for seep 6 and the total seep discharge hydrograph compare favorably (fig. 4). Subtracting the baseflow from the total seep discharge yields the predicted interflow hydrograph which is also presented in figure 4. Significant interflow events appear to be correlated with the precipitation record, suggesting that the regression model is working properly.

At the Forty Acre Well site an equally strong predictive relationship (adjusted $r^2 = 0.89$, p-value = 0.001) exists between baseflow and the water level in observation well 14.

For the period following April 1985, at which time induced alkaline recharge zones were introduced at the Forty Acre site, the predicted baseflow hydrograph for seep 7A agrees favorably with the total seep discharge (fig. 5). Prior to April 1985 the predicted baseflow is consistently greater than the observed total discharge. The model was calibrated using data following the treatment, suggesting that the hydrology of the site has been substantially modified by the reclamation efforts.

Flow Components and Seep Chemistry

The cross-correlation analysis of baseflow and acidity for the Eight Acre site shows that at zero lag time acidity is negatively correlated (-0.57) with baseflow. The correlation becomes progressively more positive with increasing lag time, reaching a peak

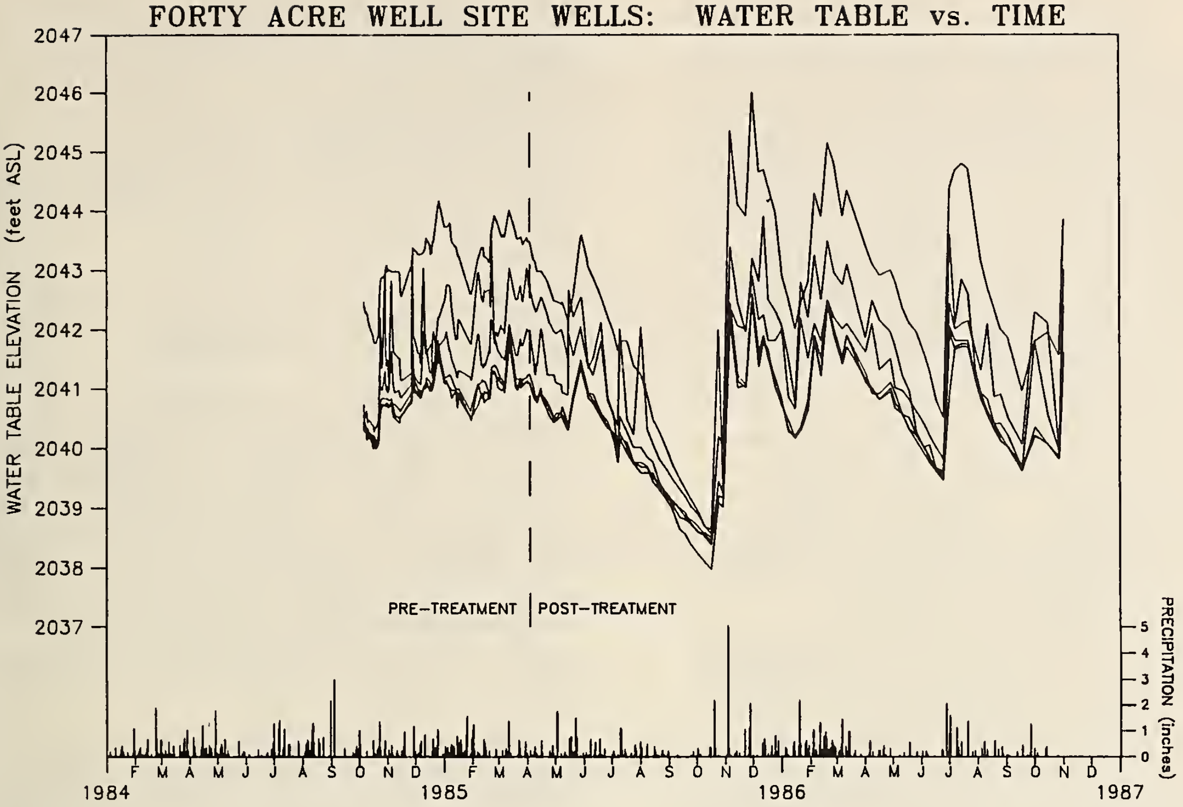

Figure 2. Water table elevations versus time and precipitation data for Forty Acre Well site.

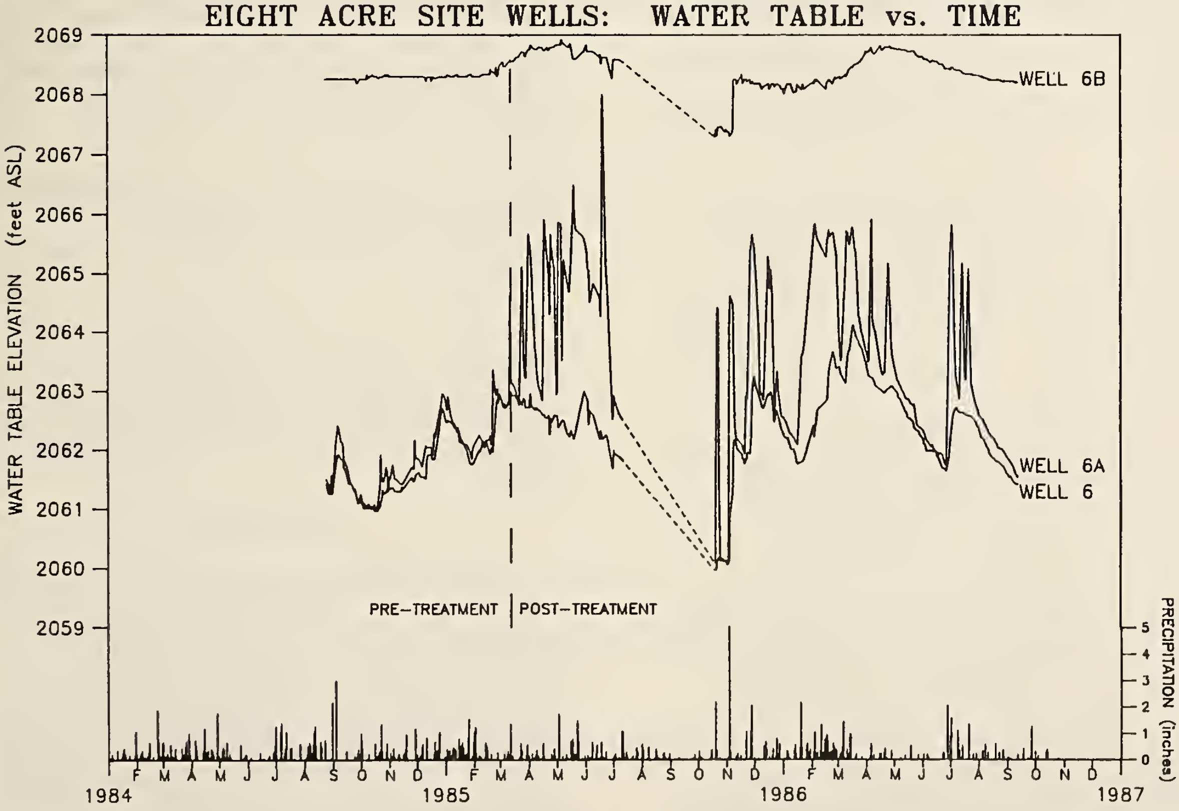

Figure 3. Water table elevations versus time and precipitation data for Eight Acre Well site.

correlation of +0.60 with a lag time of 20 weeks.

The initial inverse relationship may be the result of three effects. The first is that an increase in baseflow is usually preceded by an increase in interflow. As described below, interflow is negatively correlated with acidity and may mask the impact of baseflow. A second alternative is that the baseflow, which arrives at the seep earliest, is from meteoric waters which have infiltrated the backfill in the vicinity of the seep. The thickness of the mine-spoil through which these waters pass is relatively thin as compared with most of the Eight Acre site. Additionally, this particular part of the mine-spoil is adjacent to the outslope, which has more oxygen available to circulate and react with the acid-producing material. Therefore, the infiltrating water comes into contact with a thinner sequence of overburden material that may already be leached of its acid production potential. The third possibility is that the installation of post-holes treated with sodium hydroxide, centered around the seep, is reducing the acid production in the vicinity of the seep or neutralizing acidity.

At the Eight Acre site the strong positive correlation between baseflow and acidity which peaks at a lag of 20 weeks may represent the arrival of water that has percolated through the spoil up-gradient from the seep and flowed laterally below the water table. In this area the spoil is thicker and the oxygen circulation may be more restricted than in the spoil near the seep. These factors could prolong the acid-producing potential of this portion of the backfill and increase the acidity of the water relative to the water that passes through a thinner portion of the spoil.

A weak negative correlation (-0.26) exists between interflow and acidity at zero lag time. Though the correlation becomes slightly more negative (-0.33) over the next two lag periods, interflow is expected to have diminished by the end of the first week. The results show that interflow serves to dilute seep acidity.

Acidity to sulfate ratios, when compared with baseflow, indicate slightly higher acidity to sulfate values with increasing lag time. This may be due to a difference in the pyrite oxidation reactions.

Acidity to sulfate ratios display an inverse relationship with interflow (-0.43 at 1 week). This may indicate that some neutralization of acidity is occurring, possibly due to treatment interaction.

At the Forty Acre Well site, cross-correlation analysis shows a very weak relationship between baseflow and acidity. Initially, the correlation is negative (-0.19 at zero lag time). After 3 weeks there is a slightly positive correlation (+0.20), and at 11 weeks there is another negative peak (-0.24). The early negative correlation may be the result of causes similar to those of the Eight Acre site. The overall subdued character of the relationship between baseflow and acidity may be due either to the character of the ground water flow within the mine site or to treatment effects which will be discussed below.

There is no apparent correlation between interflow and acidity from zero lag time up to 20 lags (weeks).

At zero lag time, sulfate is negatively correlated (-0.43) with baseflow. The correlation becomes more positive and reaches a peak (+0.47) near a lag of 16 weeks. This is similar to what was observed at the Eight Acre site. Here too, the local baseflow may pass through a thin column of spoil which may be depleted of its acid production potential. The baseflow originating from more distant parts of the mine may have a higher acidity because of traversing a thicker and more reactive spoil.

There is no apparent correlation between interflow and sulfate. This suggests that the observation that acidity is not correlated with interflow is due to the lack of acid production in the unsaturated zone through which the interflow moves, rather than neutralization of the acidity.

The acidity to sulfate ratio exhibits a slight positive correlation (+0.29), with baseflow peaking at 3 weeks followed by a moderate negative correlation which reaches a peak at 13 weeks (-0.56). The inverse relationship may indicate neutralization of acidity in ground water within the backfill due to the impact of treatments or an alteration of the chemical reactions controlling the oxidation of pyrite and its reaction products.

There is no apparent correlation between acidity to sulfate ratio and interflow. There is no evidence to suggest that the interflow water quality is being modified by neutralization or an alteration of the oxidation reactions of pyrite.

CONCLUSIONS

During high-intensity, short-duration precipitation events, runoff recharges the water table by flowing through highly permeable channels in the backfill. This occurs quickly as demonstrated by the rapid response of the water table to a precipitation event (manifested by the rise of the water elevation in observation wells). Under these conditions, the rate of water movement through the unsaturated zone is from 10 to 30 ft/day (3 to 9

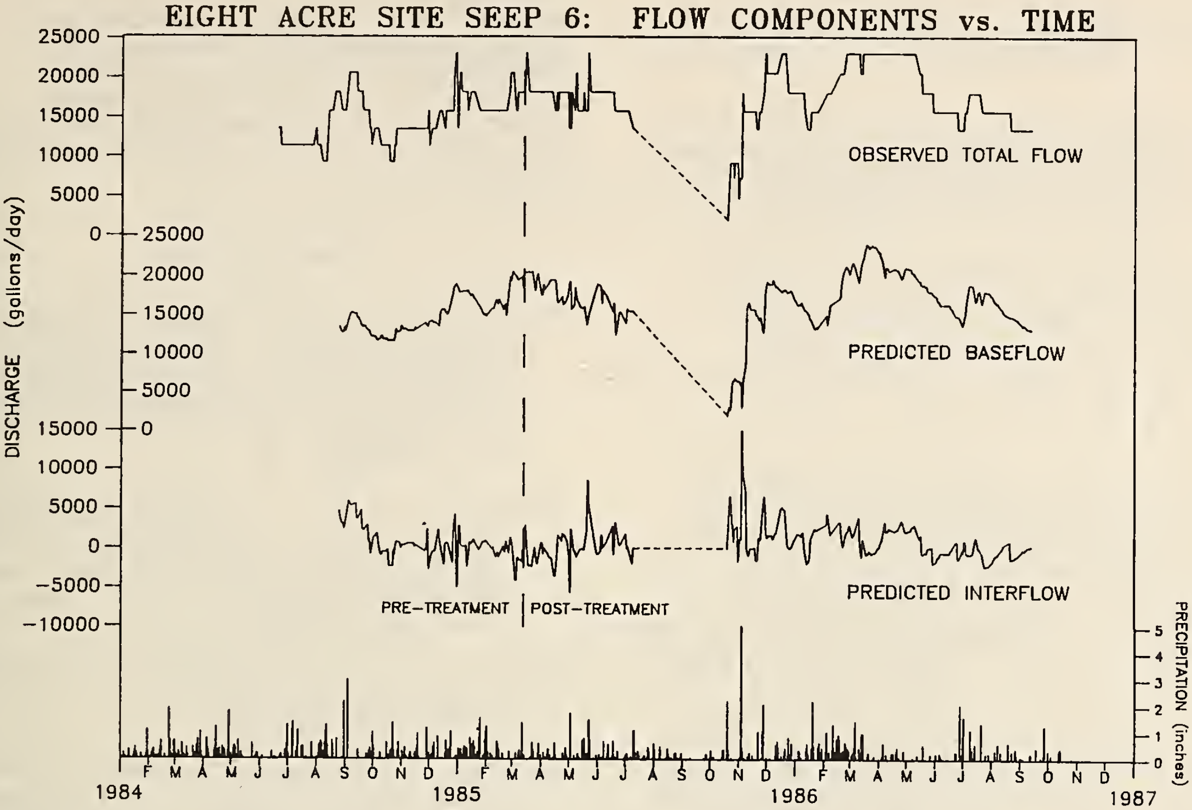
EIGHT ACRE SITE SEEP 6: FLOW COMPONENTS vs. TIME

Figure 4. Flow hydrographs of total flow, predicted base flow and predicted interflow for Seep 6, Eight Acre Site.

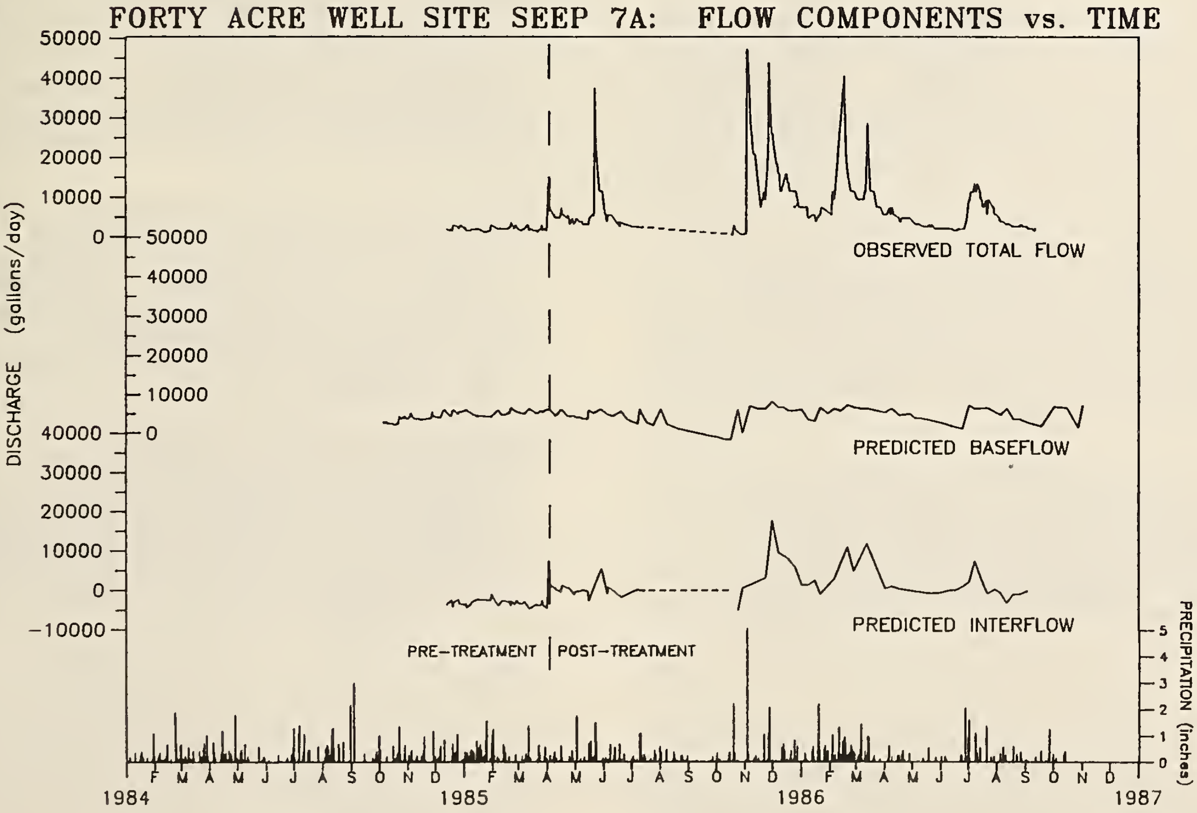
FORTY ACRE WELL SITE SEEP 7A: FLOW COMPONENTS vs. TIME

Figure 5. Flow hydrographs of total flow, predicted base flow and predicted interflow for Seep 7A, Forty Acre Site.

m/day). The speed at which the water table is recharged reflects very high hydraulic conductivity and/or channelized flow.

Further analysis of the data show the installation of induced alkaline recharge zones at both the Eight Acre and Forty Acre Well sites to have successfully modified the hydrology of the backfill.

The plastic liner covering a major portion of the Eight Acre site is not completely effective in preventing recharge of the backfill by meteoric waters due either to unlined portions of the backfill, leaks in the liner, of lateral flow.

Regression analysis was successfully used to correlate water table elevations with baseflow (sustained by deep ground water regimes) and to predict the baseflow component of the total flow. Having successfully estimated the baseflow component, it was possible to quantify the interflow (shallow lateral flow) component of a seep.

The baseflow at both the Eight Acre and Forty Acre sites promptly displays a negative correlation with acidity. This indicates that the interflow component of baseflow, which arrives at a seep first, has less acidity because it flowed through a smaller thickness of spoil and which may be leached clean of its acid-producing potential.

At both the Eight Acre and Forty Acre sites baseflow exhibits a delayed positive correlation with acidity. This suggests that baseflow, sustained by ground water from deeper parts within the mine-spoil has a higher acidity, possibly due to the greater thickness of spoil through which recharge must pass and/or a greater acid-producing potential of the spoil material. Under these conditions recharge to the backfill is by the occasional areally distributed, vertically infiltrating wetting fronts, generated by low-intensity, long-duration rains or spring thaws. Here, the entire backfill becomes saturated and a larger volume of rock material is leached.

At the Forty Acre Site interflow did not correlate with acid concentration. At the Eight Acre site interflow is negatively correlated with acidity. Therefore, the vadose zone of the backfill, through which interflow moves, does not appear to be a major acid contributor. This suggests that the acidity of the seep is sustained by a large acid reservoir, occasionally replenished by long-term vertically infiltrating waters (recharge events occurring at field capacity saturation) that commonly develop during the spring thaw.

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THE USE OF PHOSPHATE MATERIALS AS AMELIORANTS FOR ACID MINE DRAINAGE

John J. Renton, Alfred H. Stiller and Thomas E. Rymer

Abstract.--Research has shown that limestone, when used as an acid ameliorant in surface mine reclamation may result in an increase in both the acid production rate and the total acid load. Rock phosphate has been shown to be an effective acid ameliorant based upon its ability to sequester the major oxidizing agent of the iron disulphide minerals, Fe^{+3}, as an insoluble phosphate. A series of coordinated bench scale and small field scale experiments were conducted to evaluate the response of rock phosphate intermixed with toxic rock materials upon exposure to laboratory and real weathering conditions. The experiments utilized rock phosphate from granule size down to -325 mesh at application rates up to 7 wt% apatite. The work showed that rock phosphate in excess of about 1/16" mean diameter was relatively ineffective as an ameliorant. Effectiveness as an ameliorant, however, increased with decreasing particle size and application rate. Most effective was a clay slurry spiked with -325 mesh apatite and hydraulically applied. The results showed that a minimum application rate of about 1 wt% apatite is required for ameliorization to become effective and that reductions of acid production rate and total acid load can be reduced up to 90% over an untreated control at application rates of about 4 to 5 wt% apatite.

INTRODUCTION

In areas producing high sulfur coal (>1 wt% S) such as the Illinois Basin, highly calcareous overburden materials or calcite-rich surficial materials are readily available for reclamation purposes. As a result, acid mine drainage is rarely a problem. However, in high sulfur areas such as the northern Appalachian Basin where calcareous rocks are not generally abundant, limestone has been routinely added to the toxic (sulfur containing) rock materials during reclamation to ameliorate acidity. However, the use of limestone has not always resulted in the elimination of acid waters.

Early in the research of the authors, experimental weathering data indicated that the presence of calcite in sulfur-containing rock materials could actually INCREASE acid production. In initial soxhlet leach experiments designed to evaluate the acid producing potential of various coals and coal-associated rocks, a direct correlation was observed between the calcium content and INCREASING sulfate concentration (used as a measure of originally produced acidity) of the leachates. It was also observed that coals collected for study which did not have exceptionally high sulfur contents but contained iron disulphide minerals in direct contact with calcite invariably would rapidly decompose the cloth collection bags. Acid was obviously being produced at a rate disproportionate to the sulfur content of the coal.

To further investigate the effect of calcite on acid production from toxic rock materials, a series of experiments was conducted which intermixed pure calcite with several rock materials of differing toxic potential at application schedules of 0.50, 1.00, 2.00 and 4.00 wt% calcite. The experiments showed that the addition of calcite in application rates up to about 5 wt% increased acid production over that of the untreated controls (Fig. 1). Acid loads reached a maximum at about 1.0 wt% calcite addition after which acid production dropped. At about 5 wt% $CaCO_3$ addition, the acid production equaled that of the untreated controls. Beyond 5 wt% calcite addition, the acid production decreased relative to the controls, and calcite became an

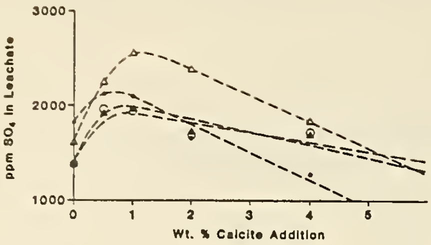


FIGURE 1. Relation Between SO_4^{-2} Production (Acid Production) from Four Typical Toxic Rock Materials Treated with Calcite at 0.5, 1.0, 2.0 and 4.0 Wt. % Addition Rates

effective acid ameliorant.

It is important to note that the use of limestone in surface mine reclamation is usually not intended to eliminate the PRODUCTION of acid from the weathering of rocks containing iron disulphide minerals but rather is meant only to neutralize acidity. It should be pointed out, however, that $CaCO_3$ will inhibit the oxidation of the iron disulphides and subsequent acid production if the application rate is high enough to raise the pH of the system to approximately pH 6-7. At this point, acid production would be reduced both by the precipitation of dissolved iron, the major oxidizing agent, and by the inhibition of iron and sulfur oxidizing bacteria.

Normally, calcite is used simply to neutralize acid already generated. Because the neutralization reaction takes place at the surface of the calcite grains, the calcite grains will eventually become coated with precipitated iron oxy-hydroxides thereby reducing the effective calcite concentration. According to the experimental data presented in Fig. 1, should the effective calcite concentration drop below 5 wt%, the system will once again become a net acid producer. This may explain the frequent lack of success in using limestone as an AMD ameliorant.

With limestone being questioned as a potential ameliorant, a substitute was sought. Our objective was to utilize a natural occurring material so as not to subject the environment to another source of unnatural pollution and preferably to utilize a material that would actually prevent the oxidation of the iron disulphide minerals rather than simply neutralize acidity. Apatite was chosen because it filled all the criteria. Apatite eliminates acid formation by removing Fe^{+3}, the major oxidizer of the iron disulphide minerals, and precipitating it as an insoluble iron phosphate below pH 5.5. In addition, apatite only dissolves when the conditions drop below pH 5.5 (ref. 1). It is therefore a time release material. The purpose of this work was to systematically evaluate the effectiveness of a variety of available phosphatic materials as acid ameliorants.

EXPERIMENTAL MATERIALS

PHOSPHATE MATERIALS: Phosphate materials were categorized for this study into three types: 1) sand to pebble sized rock phosphate, 2) fine grained (less than 150 mesh) rock phosphate and 3) dried phosphate slurry (slime). The sand to pebble sized rock phosphate, composed largely of the mineral apatite, is the material that is presently being used in the Appalachian Basin with varying amounts of success (or lack of success). The fine grained rock phosphate is the larger sized apatite that has been ground into fine particle sizes in order to increase the available reactive surface area. In this research, two sizes of ground apatite were used, one designated CODE 30 that was 95% in the size range from 150 to 250 mesh and a second material designated CODE 31 that was about 65-70% less than 325 mesh. The 150-250 mesh material was considered the finest size that could be used on-site without dust generation problems. The -325 mesh material was primarily considered as an additive to increase the apatite content and subsequent effectiveness of the dried slurry material.

The phosphatic slurry (slime) is a reject material of the phosphate mining industry. The utilization of the dried slurry was considered most important in that it was an attempt to utilize a costly refuse material of the phosphate industry to solve an equally costly problem of the coal industry. The composition of slurry material varys depending upon the geographic source. The dried slurry used in these experiments averaged 25 wt% apatite the remainder being smectite dominated clay minerals. The highly reactive clay-sized apatite content, the ability of the dried material to be reslurried and hydraulically applied, the tendency of the slurry to stick to applied surfaces and the fact that the apatite content could be increased by "spiking" with fine-grained (-325 mesh) apatite were the main attributes of the material.

TOXIC MATERIALS: The toxic materials used in this work were of two varieties. The first was a common toxic "standard" material, a typical coal cleaning plant waste which was used in both bench scale and small field scale experiments. In addition, all phosphatic materials were tested in bench scale experiments against a second suite of toxic materials which represented all of the various rock lithotypes encountered in coal mining. The second suite of rock materials provided the range of sulfur contents and acid producing potentials normally encountered in mining. The data generated by the experiments using this suite of toxic materials allowed the statistical testing of all possible interrelationships between the various phosphate addition rates and individual rock compositional and acid parameters.

EXPERIMENTAL METHODS

The experiments conducted in this work were of two types: 1) bench scale and 2) small field scale (barrel) experiments. The bench scale experiments exposed 100 gram samples of the toxic materials and toxic material/phosphatic material mixtures to the synthetic weathering conditions while the small field scale experiments exposed 300 pounds of the experimental materials to natural weathering conditions. Both procedures were reported earlier and described in detail by the authors (2,3). The experimental arrangements for each is shown in figures 2 and 3 respectively.

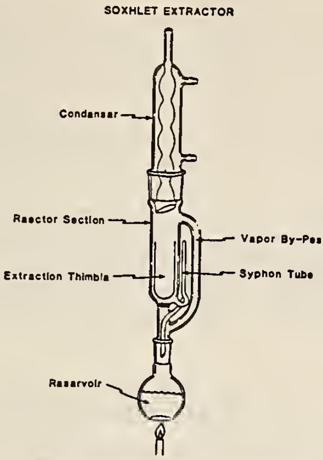


FIGURE 2. Schematic Diagram of Soxhlet Extractor

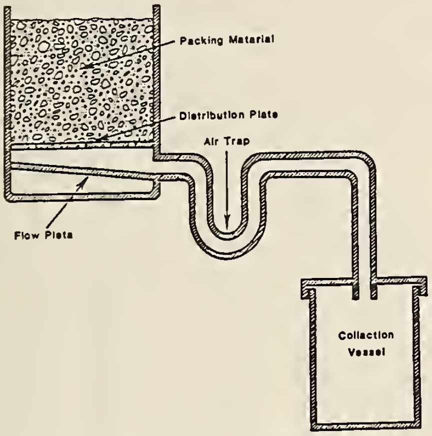


FIGURE 3. Schematic of Small Field Scale (Barrel) Experiment

TABLE 1 EXPERIMENTAL SET #1

CC#	COAL BED ASSOC.	LITHIC TYPE	St	ALPHA	S_{300}	ETA	TREATMENT	TREATMENT CC#
6434	U.FREE	REF.	2.970	-0.0003	2.56	48.00	1/4"-1/8"	5192
116	M.KITT	ROOF SHALE	1.410	-0.0012	7.578	22.495	1/4"-1/8"	5192
114	U.FREE	REF.	2.830	-0.0093	31.159	25.287	1/4"-18"	5192
22	L.KITT	REF.	2.742	-0.0012	10.778	12.405	1/4"-1/8"	5192
6434	U.FREE	REF.	2.970	-0.0003	2.56	48.00	1/8"-1/16"	5191
122	U.FREE	ROOF SHALE	7.271	+0.0075	37.347	23.894	1/8"-1/16"	5191
60	U.FREE	REF.	2.955	-0.0012	7.825	10.467	1/8"-1/16"	5191
53	U.FREE	REF.	6.501	-0.0046	26.630	25.371	1/8"-1/16"	5191
6434	U.FREE	REF.	2.970	-0.0003	2.56	48.00	<1/16"	5190
326	L.KITT	REF.	7.010	-0.0039	33.363	22.314	<1/16"	5190
35	U.FREE	REF.	1.140	-0.0019	9.957	32.649	<1/16"	5190
19	L.KITT	REF.	1.812	-0.0010	2.514	23.103	<1/16"	5190
330	U.FREE	SEAT-EARTH	2.680	-0.0068	20.415	6.263	CODE 30	5168
47	M.KITT	BONE COAL	5.263	-0.0007	19.544	23.957	CODE 30	5168
45	U.FREE	REF.	6.334	-0.0011	20.383	20.158	CODE 30	5168
40	L.KITT	PARTING	4.242	-0.0015	21.262	30.193	CODE 30	5168
6434	U.FREE	REF.	2.970	-0.0003	2.56	46.000	CODE 30	5168
337	L.KITT	REF.	9.112	-0.0051	35.064	21.617	CODE 30	5168
320	U.FREE	REF.	0.535	-0.0535	5.795	25.324	CODE 30	5168
123	U.FREE	REF.	3.196	-0.0080	19.570	16.660	CODE 30	5168
121	U.FREE	ROOF SHALE	9.740	-0.0082	13.737	24.710	CODE 30	5168
63	U.FREE	REF.	4.560	-0.0032	24.22	21.13	CODE 30	5168
55	U.FREE	ROOF SHALE	6.910	-0.0008	9.123	27.71	CODE 30	5168
24	U.FREE	OVERB. SHALE	0.652	-0.0050	4.83	5.00	CODE 30	5168
6434	U.FREE	REF.	2.197	-0.0003	2.56	46.000	AGRICO	5166
5070	U.FREE	REF.	3.150	-0.0050	17.06	58.36	AGRICO	5166
13	U.FREE	REF.	4.560	-0.0052	16.53	17.73	AGRICO	5166
12	L.KITT	ROOF SHALE	1.586	-0.0117	14.04	5.37	AGRICO	5166
19	L.KITT	REF.	1.812	-0.0010	4.777	23.103	AGRICO/C31	8348
26	U.FREE	ROOF SHALE	2.428	-0.0063	20.792	25.676	AGRICO/C31	8348
49	U.FREE	S.S.	1.740	-0.0003	1.359	45.210	AGRICO/C31	8348
62	U.FREE	REF.	5.525	-0.0050	43.102	20.943	AGRICO/C31	8348
64	U.FREE	REF.	3.312	-0.0061	27.347	15.911	AGRICO/C31	8348
119	L.FREE	PARTING	1.940	-0.0033	12.104	12.114	AGRICO/C31	8348

BENCH SCALE EXPERIMENTS

The bench scale experiments were designed to evaluate the effect of different addition schedules of each of the three basic phosphatic materials on both the rate of acid production and on the ultimmate acid load. Four sets of experiments were conducted.

SET #1:

Table 1 summarizes the first set of bench scale experiments which were conducted to evaluate the effect of intermixing the various kinds of phosphatic materials with a suite of different toxic lithotypes. In each of the experiments, the respective phosphatic material was added in 0.25, 0.50, 1.00 and 2.00 wt% apatite. All data were compared to an untreated control. All experiments were run in triplicate. The table lists the coal bed association, the specific lithotype and the various acid evaluation parameters for each of the toxic materials. The CC#'s are laboratory identification numbers.

The first 12 experiments listed are the sand to pebble sized rock phosphate separated into the indicated categories. As previously indicated, the "CODE 30" material is the rock phosphate in the size range from 150 to 250 mesh and the material indicated "CODE 31" is the same material ground to pass 325 mesh. The CODE 30 and CODE 31 materials were acquired from Texasgulf Sulfur at Aurora, North Carolina. The material termed "AGRICO" is a solar dried slurry (slime) acquired from the AGRICO Mining Co., Mulberry, Florida.

The results of the experiments were compared by plotting percent acid reduction relative to the control versus the wt% apatite addition. The data were extrapolated by computer to 5 wt% apatite addition.

SET #2:

Based upon the success of the initial experiments, a second set of experiments was conducted utilizing the AGRICO slurry material with and without CODE 31 addition intermixed as a water slurry and run against a common toxic material. The experiments are summarized in Table 2. Each wt% apatite addition with the exception of 7.00 wt% apatite was conducted using two different slurry mixtures. All experiments were conducted in triplicate. Based on the results of these experiments, two final sets of experiments were designed.

TABLE 2 EXPERIMENTAL SET #2

	SOLID MIX			SLURRY MIX	
CC#	gm AGRICO	gm CODE 31	ml/H_2O	gm SOLID MIX	WT% APATITE ADDITION
8342	5	0	50	5	0.25
8343	260	13	200	40	2.00
8344	260	13	750	225	1.25, 1.75, 3.25, 3.50, 3.75, 4.00
8345	300	60	300	60	0.75, 2.25, 2.75
8346	300	60	1000	300	2.75, 3.25, 4.00, 4.50
8347	450	225	750	75	0.25, 0.50, 1.00, 1.25, 1.50, 1.75, 2.50
8348	450	225	750	150	0.50, 1.00, 2.00, 2.50, 3.00, 3.50, 5.00
8349	450	225	1500	450	0.75, 1.50, 2.25, 3.00, 3.75, 4.50, 5.00, 7.00

SET #3:

In this set of experiments, slurry CC# 8348, a 1:0.5 blend of dried slurry CODE 31 apatite was intermixed with four different toxic materials at application schedules of 1, 2, 3 and 4 wt% apatite (see Table 3).

TABLE 3 EXPERIMENTAL SET #3

AGRICO VS. 6 DIFFERENT TOXIC MATERIALS

CC#	COAL	ROCK TYP.	St	ALPHA	S300	ETA
26	U.FREE	ROOF SH.	2.418	0.0065	21.325	25.676
62	U.FREE	PREP.REF.	5.525	0.0050	28.397	20.943
64	U.FREE	PREP.REF.	3.312	0.0061	17.741	15.911
119	L.FREE	PARTING	1.940	0.0033	13.976	12.114

CC# 8348 SLURRY
450 gm AGRICO + 225 gm CODE 31
750 ml H_2O + 150 gm MIXTURE

APPLICATION SCHEDULE
CONTROL, 1 wt%, 2 wt%, 3 wt% and 4 wt% APATITE

SET #4:

Initially, the CODE 30 material was tested against a variety of toxic lithotypes. In the fourth set of experiments, the CODE 30 material was intermixed with the previously utilized common toxic lithotype in application schedules ranging from 0.50 wt% to 5.00 wt% at 0.25 wt% intervals.

The entire bench scale experimental effort consisted of a total of 3285 individual experiments with 65,700 analyses. This point is made only to emphasize the fact that the database is sufficiently large to allow a reasonably high statistical reliability to be assigned to any effectivity comparisons that will be made.

SMALL FIELD SCALE (BARREL) EXPERIMENTS

The second phase of this work involved small field scale (BARREL) experiments. The primary objectives of this study were twofold: 1) to determine the effect of phosphate mine waste on acid production from bituminous mine waste rock under natural conditions of weathering and 2) to provide the data needed to calculate conversion factors to allow bench scale data to be related to real weathering situations. The fact that phosphate rock can significantly reduce the production of AMD had already been established by the authors by previous experimentation. However, statistical analysis of the data showed that the effectiveness of phosphate was not directly related to any stoichiometric formulation based on the percentage of pyrite in the rock sample. Therefore, the ameliorative property of phosphate must be mass transfer controlled. This being the case, the sample treated with the smaller particle size, but equal application rate of rock phosphate will be more effective as an ameliorant.

The soxhlet experiments tested the effectiveness of surface area and weight percent of phosphate on 100 gram samples of toxic material. Because of the simplicity of this experimental procedure, large numbers of experiments can be run and a large data base can be accumulated. The question that yet remained to be answered was how these soxhlet tests related to actual atmospheric weathering.

The toxic materials used in these experiments were of two types: 1) a cleaning plant waste from Grant County, West Virginia, the toxic "standard" material and 2) a sandstone overburden rock of the Kittanning coal bed in central West Virginia. Compared to many toxic rock wastes studied over the past four years, the cleaning plant waste material is of average toxicity. The Kittanning coal beds are some of the most extensive in the state. As a result, the mining community must frequently contend with the sandstone overburden material. Sixteen tons of each material were obtained and screened to a top size of 1.5" in order to guarantee that when packed into the plastic containers, the water would not channel through the barrels but rather would travel downward in a uniform front.

Identical sets of the samples and corresponding treatments used in the field scale experiments were prepared and evaluated by the soxhlet bench scale procedure experiments to provide the data by which the field scale and bench scale data could be correlated.

Based upon the finding from the bench scale experiments that rock phosphate particle sizes greater than 1/16" showed limited ameliorative effectiveness, only to fine sizes were used in the barrel experiments. For the small field scale experiments, the Code 30 and 31 materials were further sub-sized into four seive size ranges: 1) 18-35 mesh, (750 microns), 2) 36-60 mesh, (375 microns, 3) 60-120 mesh (187 microns), and 4) less than 120 mesh (125 microns).

A total of ninety field scale barrel experiments were prepared (see Table 4). Each experi-

TABLE 4 SMALL FIELD SCALE (BARREL) EXPERIMENTS

MATERIAL	AMELIORANT	PARTICLE MESH SIZE	APPLICATION RATE	REP	EXPER. NUMBER
REFUSE	P-ROCK	18-35	1.20%	1	01
REFUSE	P-ROCK	18-35	1.20%	2	02
REFUSE	P-ROCK	18-35	1.20%	3	03
REFUSE	P-ROCK	18-35	0.40%	1	04
REFUSE	P-ROCK	18-35	0.40%	2	05
REFUSE	P-ROCK	18-35	0.40%	3	06
REFUSE	P-ROCK	18-35	0.13%	1	07
REFUSE	P-ROCK	18-35	0.13%	2	08
REFUSE	P-ROCK	18-35	0.13%	3	09
REFUSE	P-ROCK	18-35	0.04%	1	10
REFUSE	P-ROCK	18-35	0.04%	2	11
REFUSE	P-ROCK	18-35	0.04%	3	12
REFUSE	P-ROCK	35-60	1.20%	1	13
REFUSE	P-ROCK	35-60	1.20%	2	14
REFUSE	P-ROCK	35-60	1.20%	3	15
REFUSE	P-ROCK	35-60	0.40%	1	16
REFUSE	P-ROCK	35-60	0.40%	2	17
REFUSE	P-ROCK	35-60	0.40%	3	18
REFUSE	P-ROCK	35-60	0.13%	1	19
REFUSE	P-ROCK	35-60	0.13%	2	20
REFUSE	P-ROCK	35-60	0.13%	3	21
REFUSE	P-ROCK	35-60	0.04%	1	22
REFUSE	P-ROCK	35-60	0.04%	2	23
REFUSE	P-ROCK	35-60	0.04%	3	24
REFUSE	P-ROCK	60-120	1.20%	1	25
REFUSE	P-ROCK	60-120	1.20%	2	26
REFUSE	P-ROCK	60-120	1.20%	3	27
REFUSE	P-ROCK	60-120	0.40%	1	28
REFUSE	P-ROCK	60-120	0.40%	2	29
REFUSE	P-ROCK	60-120	0.40%	3	30
REFUSE	P-ROCK	60-120	0.13%	1	31
REFUSE	P-ROCK	60-120	0.13%	2	32
REFUSE	P-ROCK	60-120	0.13%	3	33
REFUSE	P-ROCK	60-120	0.04%	1	34
REFUSE	P-ROCK	60-120	0.04%	2	35
REFUSE	P-ROCK	60-120	0.04%	3	36
REFUSE	P-ROCK	LT 120	1.20%	1	37
REFUSE	P-ROCK	LT 120	1.20%	2	38
REFUSE	P-ROCK	LT 120	1.20%	3	39
REFUSE	P-ROCK	LT 120	0.40%	1	40
REFUSE	P-ROCK	LT 120	0.40%	2	41
REFUSE	P-ROCK	LT 120	0.40%	3	42
REFUSE	P-ROCK	LT 120	0.13%	1	43
REFUSE	P-ROCK	LT 120	0.13%	2	44
REFUSE	P-ROCK	LT 120	0.13%	3	45
REFUSE	P-ROCK	LT 120	0.04%	1	46
REFUSE	P-ROCK	LT 120	0.04%	2	47
REFUSE	P-ROCK	LT 120	0.04%	3	48
REFUSE	P-SLURRY	------	4.80%	1	49
REFUSE	P-SLURRY	------	4.80%	2	50
REFUSE	P-SLURRY	------	4.60%	3	51
REFUSE	P-SLURRY	------	1.60%	1	52
REFUSE	P-SLURRY	------	1.60%	2	53
REFUSE	P-SLURRY	------	1.60%	3	54
REFUSE	P-SLURRY	------	0.52%	1	55
REFUSE	P-SLURRY	------	0.52%	2	56
REFUSE	P-SLURRY	------	0.52%	3	57
REFUSE	P-SLURRY	------	0.16%	1	58
REFUSE	P-SLURRY	------	0.16%	2	59
REFUSE	P-SLURRY	------	0.16%	3	60
REFUSE	CONTROL	------	-----	1	61
REFUSE	CONTROL	------	-----	2	62
REFUSE	CONTROL	------	-----	3	63
SANDSTONE	P-ROCK	18-35	0.40%	1	70
SANDSTONE	P-ROCK	18-35	0.40%	2	71
SANDSTONE	P-ROCK	18-35	0.40%	3	72
SANDSTONE	P-ROCK	35-60	0.40%	1	73
SANDSTONE	P-ROCK	35-60	0.40%	2	74
SANDSTONE	P-ROCK	35-60	0.40%	3	75
SANDSTONE	P-ROCK	35-60	0.40%	1	76
SANDSTONE	P-ROCK	35-60	0.40%	2	77
SANDSTONE	P-ROCK	35-60	0.40%	3	78
SANDSTONE	P-ROCK	LT 120	0.40%	1	79
SANDSTONE	P-ROCK	LT 120	0.40%	2	80
SANDSTONE	P-ROCK	LT 120	0.40%	3	81

SANDSTONE	P-SLURRY	------	4.80%	1	82
SANDSTONE	P-SLURRY	------	4.80%	2	83
SANDSTONE	P-SLURRY	------	4.80%	3	84
SANDSTONE	P-SLURRY	------	1.60%	1	85
SANDSTONE	P-SLURRY	------	1.60%	2	86
SANDSTONE	P-SLURRY	------	1.60%	3	87
SANDSTONE	P-SLURRY	------	0.52%	1	88
SANDSTONE	P-SLURRY	------	0.52%	2	89
SANDSTONE	P-SLURRY	------	0.52%	3	90
SANDSTONE	P-SLURRY	------	0.16%	1	91
SANDSTONE	P-SLURRY	------	0.16%	2	92
SANDSTONE	P-SLURRY	------	0.16%	3	93
SANDSTONE	CONTROL	------	-----	1	94
SANDSTONE	CONTROL	------	-----	2	95
SANDSTONE	CONTROL	------	-----	3	96

ment consisting of three hundred pounds of toxic material with the appropriate phosphate ameliorant. The barrels were placed on 8 benches, with 12 experiments per bench; the placement of individual experiments was determined by random number generation.

TREATMENT OF THE DATA

The basic data collected from the leachates of both the bench scale and small field scale experiments included pH before and after the addition of hydrogen perioxide, specific conductivity, acidity, the concentrations of Ca, Mg, Na, K, Fe, Mn, Al, Si and sulfate. The sulfate concentration was used as a measure of original acid production and was tabulated in cumulative milligrams of sulfate after each cycle of the bench scale experiments. From these data and the initial sulfur content of the rock material, a percent unreacted sulfur (%Su) remaining within the rock material after each leachate collection was calculated.

Because laboratory leaching and field leaching were conducted under totally different experimental conditions, it was necessary to equate a 14 day soxhlet cycle to the actual field days of the barrel experiments. To accomplish this, the number of field days required to reduce the sulfur content of the rock material to the same percent unreacted sulfur (%Su) for each of the four cycles of the bench scale data were calculated. These data were plotted versus the corresponding times for the bench scale data (figure 4). A regression relationship was used to calculate the real time days required to achieve the corresponding %Su observed in the laboratory experiments. The results showed that one 14-day laboratory cycle was equal to 8.8 real time days. The ratio 8.8/14 was therefore the scaling factor which allowed all subsequent bench scale data to be equated relative to real time.

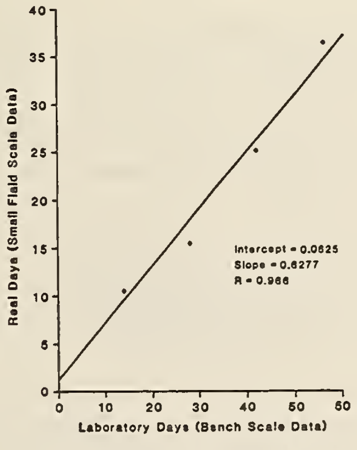


FIGURE 4. Time to Reduce % S to Equal Concentrations of Unreacted Sulphur

EXPERIMENTAL PARAMETERS

Previous research by the authors had established four experimental parameters which were used to evaluate the toxic potential of an acid producing system: 1) an acid production rate constant, ALPHA, which is the slope of the plot of the naturallogarithm of the percent of unreacted sulfur of the toxic material versus real time (see fig. 5) 2) a sulfate production parameter, S300, which is the calculated amount of sulfate produced from 1000 Tons of toxic material in 300 days. This parameter is used as a comparison statistic, 3) the ACID Load which is the equivalent amount of $CaCO_3$ Tons of the toxic material and 4) a parameter ETA, which is calculated by dividing the acid load generated from 1000 Tons of the toxic material by the total sulfur content of the toxic material.

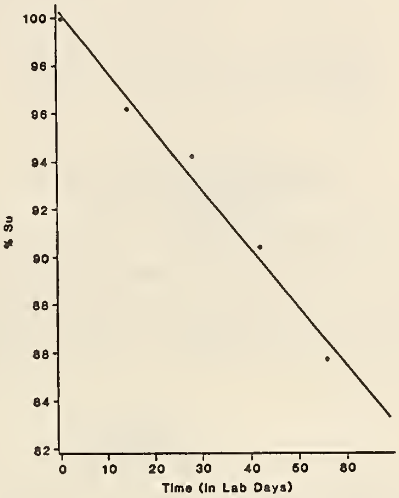


FIGURE 6. Percent Unreacted Sulphur (%Su) Versus Time in Lab Days for Bench Scale Experiments

RESULTS OF THE INVESTIGATION

Bench Scale Experiments

The results of the investigation are quite clear. The effectiveness of the rock phosphate is simply a question of mass transfer; the effectiveness increasing with decreasing particle size and increasing magnitude of the application rate.

The results of experimental SET #1 are illustrated in Figure 6. The toxicity parameters for the rock material used in the individual experiments is indicated on the figure for each particle size experiment. It is significant to note that the sand to pebble-sized material is relative ineffective at acid reduction. Even the -1/16" size does not reduce the acid load by 50% at projected application schedules of 5 wt%.

The CODE 30 material, as would be expected was significantly more effective with 8 out of 12 experiments resulting in a 50% acid reduction with an average application schedule of about 2.2 wt% apatite. Of the remaining 4 experiments which showed relatively low response, the sulfur content of the toxic material in two of the experiments was in excess of 9 wt%, thereby explaining the limited response.

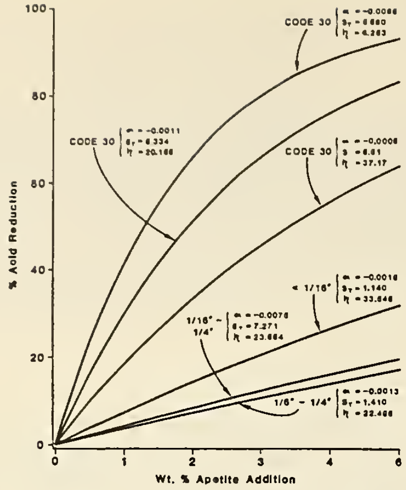


FIGURE 6. Percent Acid Reduction vs. Wt. % Apatite Application for Various Sized Rock Phosphate Materials

Most encouraging, however, were the results of experiment SETS #2 and #3 which utilized the dried slurry material. Because the material contained only about 25% by weight apatite, the effectiveness of the material used without any apatite addition was limited (fig. 7). However, with the addition of CODE 31 material, the slurry material showed significant improvement in performance. The results of experimental SET #2 are summarized in figures 8 and 9 which plot acid load and alpha reduction versus wt% apatite addition respectively.

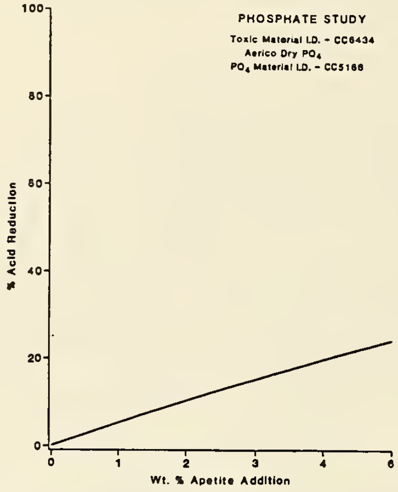


FIGURE 7. Percent Acid Reduction vs. Wt. % Apatite Application for Dried Slurry - No Code 31 Spike

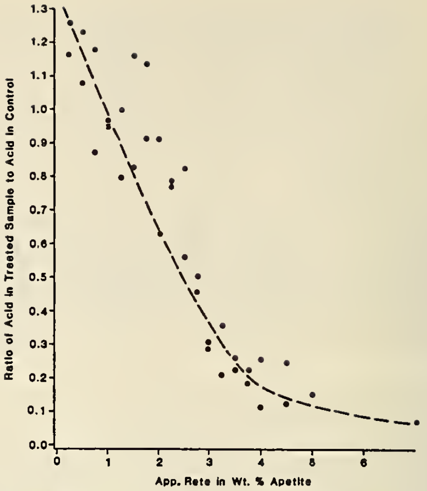


FIGURE 8. Percent Acid Reduction vs. Wt. % Apatite Application for Dried Slurry with Code 31 Spike

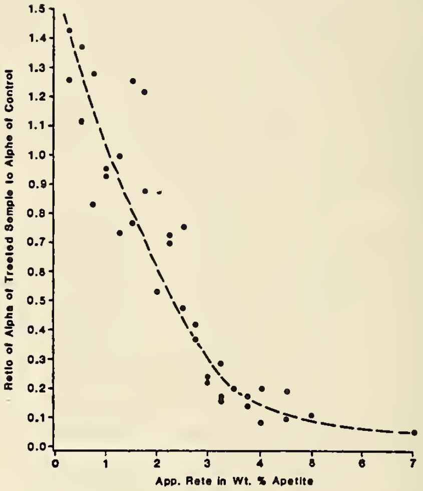


FIGURE 9. Percent Alpha Reduction vs. Wt. % Apatite Application for Dried Slurry with Code 31 Spike

The data show that approximately 0.9 wt% apatite must be added before acid reduction is initiated. Below 0.9 wt% apatite addition, the chemical effect of calcium on the system is apparently the same as observed for calcite addition, namely, it results in an increase in acid production. Between 0.9 wt% and 4.0 wt% apatite addition, however, reduction in acid production is rapid. Note that on the average, an application schedule of 5 wt% apatite reduced both acid load and the rate of acid production by more than 90% relative to the untreated control. As previously shown, calcite must be added at a 5 wt% addition schedule simply to INITIATE positive acid reduction.

The results from the slurry-CODE 31 mixtures of experiment SET #3 are illustrated in figures 10 through 17 and the data from SET #4, the CODE 30 addition to the "standard" prep refuse, are shown in figures 18 and 19. The trends in these data are similar to those of the previous experiments.

FIGURE 10

ROCK TYPE - ROOF SHALE
STRATIGRAPHY - UPPER FREEPORT
TOTAL SULFUR - 2.410
ALPHA - 0.0065
ETA - 25.7
PHOSPHATE ID - CC 8348
SLURRY: CODE31 RATIO 1:0.8

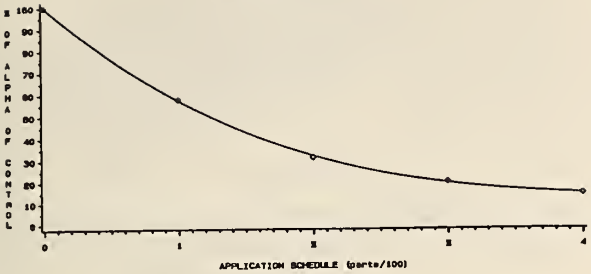


FIGURE 11

ROCK TYPE - ROOF SHALE
STRATIGRAPHY - UPPER FREEPORT
TOTAL SULFUR - 2.410
ALPHA - 0.0065
ETA - 25.7
PHOSPHATE ID - CC 8348
SLURRY: CODE31 RATIO 1:0.0

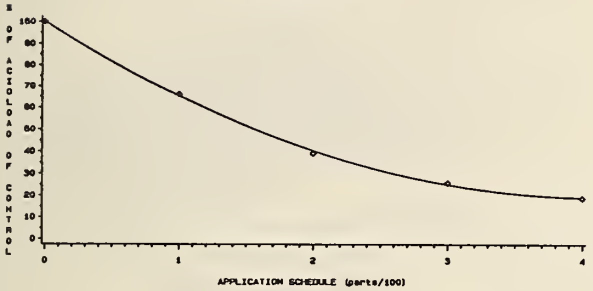


FIGURE 12

ROCK TYPE - PREP REFUSE
STRATIGRAPHY - UPPER FREEPORT
TOTAL SULFUR - 0.825
ALPHA - 0.005
ETA - 20.94
PHOSPHATE ID - CC 8348
SLURRY: CODE31 RATIO 1:0.0

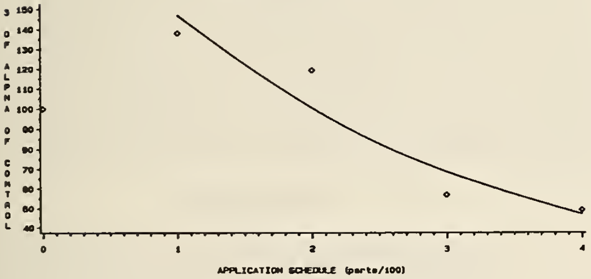


FIGURE 13

ROCK TYPE - PREP REFUSE
STRATIGRAPHY - UPPER FREEPORT
TOTAL SULFUR - 0.525
ALPHA - 0.005
ETA - 20.94
PHOSPHATE ID - CC 8348
SLURRY: CODE31 RATIO 1:0.8

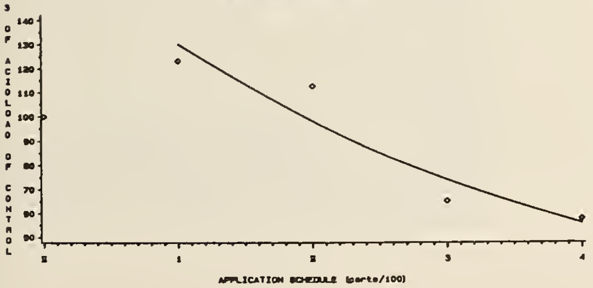


FIGURE 14

ROCK TYPE - PREP REFUSE
STRATIGRAPHY - UPPER FREEPORT
TOTAL SULFUR - 3.312
ALPHA - 0.000
ETA - 12.114
PHOSPHATE ID - CC 8348
SLURRY: CODE31 RATIO 1:0.0

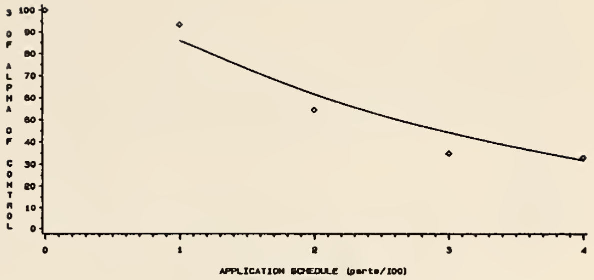


FIGURE 15

ROCK TYPE - PREP REFUSE
STRATIGRAPHY - UPPER FREEPORT
TOTAL SULFUR - 3.312
ALPHA - 0.006
ETA - 12.114
PHOSPHATE ID - CC 8348
SLURRY: CODE31 RATIO 1:0.0

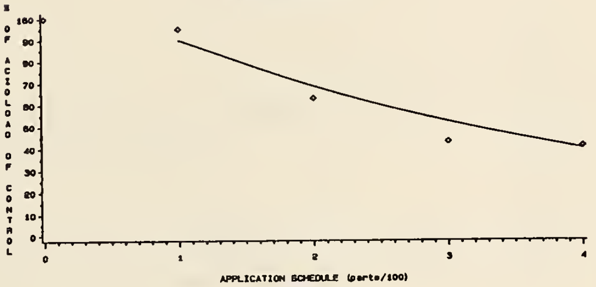


FIGURE 16

ROCK TYPE - SHALE PARTING
STRATIGRAPHY - LOWER FREEPORT
TOTAL SULFUR - 1.040
ALPHA - 0.0033
ETA - 12.1
PHOSPHATE ID - CC 8348
SLURRY: CODE31 RATIO 1:0.0

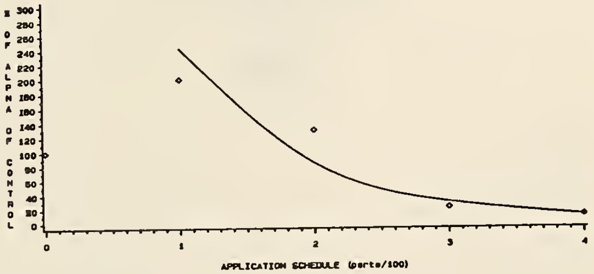


FIGURE 17

ROCK TYPE - SHALE PARTING
STRATIGRAPHY - LOWER FREEPORT
TOTAL SULFUR - 1.040
ALPHA - 0.0033
ETA - 12.1
PHOSPHATE ID - CC 8348
SLURRY: CODE31 RATIO 1:0.0

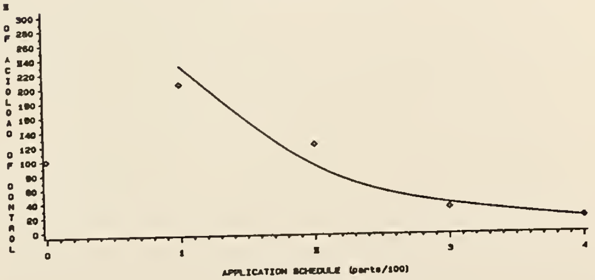


FIGURE 18

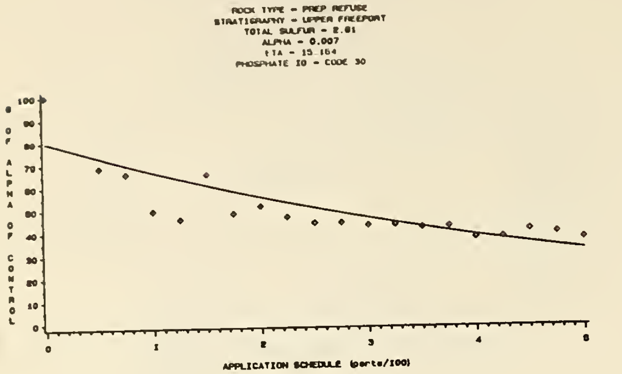
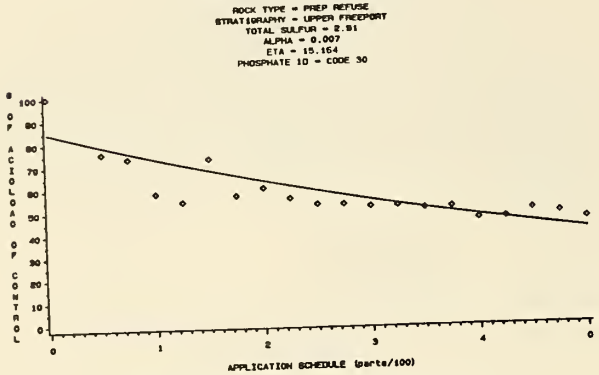


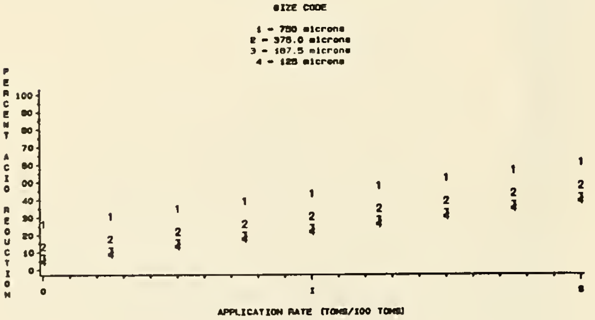
FIGURE 19



SMALL FIELD SCALE EXPERIMENTS

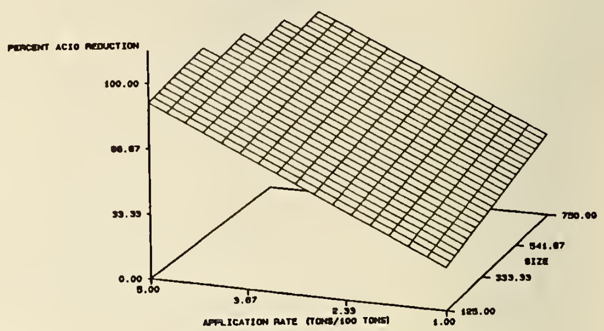
The results of the small field scale experiments are shown in figures 20 through 21A. Similar to the bench scale experiments, the data show the ameliorative effectiveness to increase with decreased particle size. The three dimensional plot in figure 21 shows however, that when dealing with fine particle sizes, the application schedule is more influential on ameliorative effectiveness than is particle size. Statistically, the ameliorative reaction of all the fine sizes tested was similar. Most significant is that both the bench scale and field scale sets of experiments show that maximum ameliorative effectiveness of rock phosphate is achieved at about 4 wt% apatite addition.

FIGURE 20



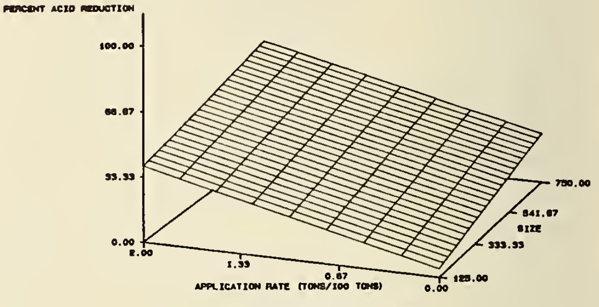
VARIOUS PHOSPHATE PARTICLE SIZE
EFFECTS ON ACID PRODUCTION
OF A SINGLE TOXIC MATERIAL

FIGURE 21



SURFACE SHOWING RELATION OF PARTICLE SIZE
AND APPLICATION SCHEDULE WITH ACID PRODUCTION

FIGURE 21-A



SURFACE SHOWING RELATION OF PARTICLE SIZE
AND APPLICATION SCHEDULE WITH ACID PRODUCTION

CONCLUSIONS

1) Rock phosphate (apatite) is an effective AMD ameliorant when used in particle sizes less than 18 mesh (750 microns) and with application rates in excess of about 1wt%.
2) Maximum ameliorative effectiveness will be achieved using fine ground rock phosphate at an addition rate of about 4 or 5 wt%.
3) Below a particle size of 18 mesh, the particle size of rock phosphate becomes less important than the application rate in acid reduction.
4) The clay slurry spiked with -375 mesh apatite is an extremely effective AMD ameliorant.
5) Bench scale experiments can effectively evaluate and predict the response of toxic materials or combinations of toxic materials and ameliorants exposed to atmosphere weathering.

ACKNOWLEDGEMENTS

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A COMPUTER SIMULATION PROBABILITY MODEL FOR GEOCHEMICAL PARAMETERS ASSOCIATED WITH COAL MINING OPERATIONS

Thomas E. Rymer II, John J. Renton, and Alfred H. Stiller[2]

Abstract.--There have been many attempts to empirically model the environmental effects of various geochemical parameters associated with mining. Each of these attempts has encountered the single greatest barrier of any empirical approach; the randomness of data. Randomness manifests itself in many forms from the degree of variability within a specific dataset to the degree of intrinsic error associated with the measurement of certain variables. There are simply too many random processes, variables, and interrelations associated with a coal mine site to allow the depiction of any environmental response within reasonable certainty using only basic scientific principles, equations, and empirical formulae. Computer simulation modeling provides an effective mode of evaluating the intrinsics of such a random system. In order to generate a random probability simulation model, it is necessary to isolate pertinent elements of the system, which in this case are sulfate concentration, effluent flow, and kinetic rock properties. Some logistical set of formulated interactive governing rules must be then devised whereby the model can be limited to those aspects of the system which are deemed to be pertinent to the analysis and types of solutions for which answers are sought, which in this case is simultaneous pyrite oxidation-sulfate elimination. Within the context of this logic, a quantifiable ratio between the rate of acid generation within a mining system and the rate of acid elimination from the system has been derived. With this information in hand it is now possible to project the longevity of acid effluent from a mining operation, develop better treatment or ameiloration strategies, and determine the chemical impact of these mining operations on the immediate localized watershed.

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INTRODUCTION

A mathematical model is an attempt to quantify a specific parameter associated with a system on the basis of other measurable variables. The majority of such models deal with limited aspects of mining such as hydrological predictions, level of acid generation, or acid amelioration. Most of the models can be classified as being empirical; that is, a model dealing with variables simplified to standard regression formulae which usually have a basis in some standard chemical or engineering principle. A macromodel on the other hand, is a model which draws conclusions or predictions based on the entire mine operation with all of its interrelations and interactions.

Two important criteria exist concerning error and randomness and how these factors can effect the success of an empirical model:

1) THE MODEL MUST BE ABLE TO ABSORB THE INTRINSIC AND INHERENT ERROR OF THE SYSTEM

The model cannot be so filled with variables, constants, and complexities that the sum total of intrinsic error encountered in the measurement of the individual component variables and the error inherent in any subsequently predicted parameters becomes disguised in the form of high uncertainty. The inclusion into the model of any single variable or group of variables for which there exists a potentially high intrinsic error of measurement for the sake of higher statistical significance cannot be justified.

2) IT MUST BE ABLE TO MINIMIZE RANDOMNESS

The model may be highly dependent on variables which are random by their own nature. This randomness must be absorbed into the model and thus be reduced rather than subtly concealed in a region of high uncertainty brought about by the randomness.

A large-scale macromodel for mining operations seems to have eluded empirical modeling attempts. One need look no further than the two model qualifiers previously listed to discover the reasons; namely randomness and variable error.

Randomness and Mining Operations

Sources of randomness in an acid producing mining system can be found everywhere. Some of the sources show high levels of randomness while others will show low levels of randomness. A few of the highly variable parameters are summarized below:

1) THE VARIABILITY FOUND IN THE PERCENT TOTAL SULFUR OF INDIVIDUAL OVERBURDEN LITHOTYPES

2) EFFLUENT FLOW MEASUREMENT

3) CHEMICAL CONCENTRATION VS EFFLUENT FLOW The plot shown in figure 1 illustrates a mathematically random relationship between effluent sulfate concentration and flow

4) CLIMATIC FACTORS

5) TURBIDIMETRIC SULFATE ANALYSIS used as the measure of a acid generated

6) VARIABILITY OF PYRITE AS DETERMINED BY X-RAY DIFFRACTION ANALYSIS

7) VARIABILITY OF THE KINETIC RATE CONSTANT FOR PYRITE OXIDATION

8) VARIABILITY IN THE ACTUAL CHEMICAL MODEL

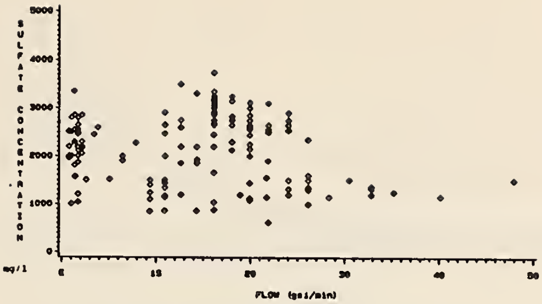

Figure 1. Random nature of sulfate concentration vs flow. Data from site DLM 135-78.

DESCRIPTION OF RESEARCH

A Random Probability Simulation Model

An alternative solution to the problems synonomous with empirical modeling is to develop a logical, quantifiable model that absorbs both randomness and error. Such a modeling scheme exists in Probability Simulation Modeling (PSM). In this type of predictive modeling, the randomness of the data itself and the error associated with individual measurements are both absorbed into the probability distribution of the data. The difference between the PSM approach and empirical modeling is that in PSM modeling the DISTRIBUTION of the data rather than the magnitude of INDIVIDUAL data points form the working data set.

One needs then to develop a logical set of rules to govern the relationship of the data distribution and any experimental parameter of interest. It is therefore possible to evaluate the effects of numerous possible combinations of parameter values (data randomness) that exist in their respective distributions.

Two important properties of a PSM are:

1) the scientific or mathematical principles governing the system have been obeyed and,
2) the statistical integrity of the original data is upheld.

The objective of this work was to develop a model which would focus on the two basic processes: 1) the production of acid within a minesite and 2) the elimination of the acid from the system. A well-established mathematical formulation known as Simultaneous Species Production-Elimination (SSPE) exists that logically describes a system. In essence, this principle states that the change in the rate of the appearance and disappearance of any species from a system is given by the differential.

$$\frac{dS}{dt} = aS(t) - bS(t) \qquad \text{(EQUATION 1)}$$

This mathematical relationship states that the rate of change with time of any chemical parameter, (S), is equal to the rate of production of S, (a), times the amount of S present at some time (t), minus the rate of elimination of S, (b), times the amount of S present at the same time, t.

This differential equation is then solved to yield a working mathematical relation:

$$S(t) = \frac{a S_0}{(b - a)} \left(e^{-at} - e^{-bt} \right) \qquad \text{(EQUATION 2)}$$

This is a member of a series of differential equations called the "Bateman Equations', after the man who derived them.

The rate constants a and b will subsequently be referred to as alpha and beta, respectively.

The SSPE model is utilized quite frequently in the study of natural systems such as the determination of the abundance of an intermediate radioactive isotope in a breakdown sequence, biochemical assimilation of hormones, and in the study of the potential effects of toxic wastes on biological systems.

The SSPE equation offers an excellent governing principle for a systems model that will allow the monitoring of pyrite oxidation products (including acid effluent) associated with a mining operation. The analogies to radioactive decay and biochemical production assimilations are parallel. In a mining operation, acid is formed as pyrite oxidizes to sulfate at a rate alpha. As a result of ground water movements, the sulfate is removed from the minesite at a rate beta. The overall process can be written:

$$FeS_2 \xrightarrow{\text{alpha}} SO_4^{-2} \text{ (in site)} \xrightarrow{\text{beta}} SO_4^{-2} \text{ (effluent)}$$

Once the values of alpha and beta (production and elimination) of the sulfate species are known, questions concerning the products of pyrite oxidation that can be answered include:

1. How fast are they being formed?
2. How fast are they being eliminated?
3. How long will the acid-producing process last?
4. What will be the effect on the system of a reduction in the magnitude of alpha as a result of the incorporation of an ameliorant?

These are questions that need to be addressed in order to solve the problems of acid mine drainage (AMD), but are questions that cannot be answered using empirical models without the introduction of large uncertainties. However, through a probability simulation analysis, solutions to such problems can be found.

The Generalized Concept of AMD as a SSPE System

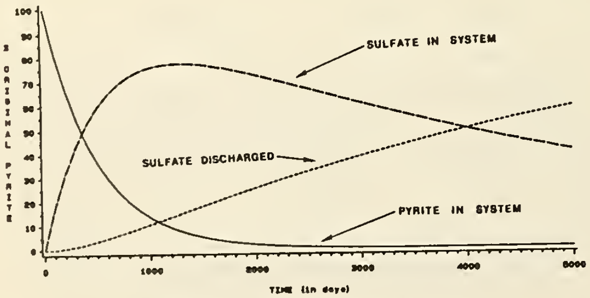

Figure 2. The pyrite-sulfate system showing the three prominent stages of sulfur species according to SSPE.

Figure 2 shows the percentage of original pyritic sulfur available in a mining system that through time exists as either unreacted pyrite, sulfate built up in the minesite, or discharged from the minesite as effluent. Note that there is a buildup of the products of oxidation (sulfate) in the system from the outset. The magnitude of alpha will determine the rate at which these oxidation products are generated. Conversely, beta is the prime indicator of the extent to which these products are being flushed from the system. It is, therefore, the ratio of alpha to beta that provides a complete insight into the buildup of oxidation products in the system. The equation tends to show that the time required for pyrite oxidation is short compared to the time required to flush the oxidation products from the system. The PSM provides a means to quantify these observations.

The Development of a Simulation Model

The goal of a simulation is to provide a mathematical procedure that will:

1) be able to utilize analytical data to predict parameters of an acid-producing system,
2) be as unaffected as possible by data randomness,
3) adhere to sound scientific principles, and
4) reproduce the statistical distribution observed in actual field data.

In order to develop such a simulation, it is necessary to know:

1) mine size and geometry,
2) field sulfate concentration and flow measurements of the effluents, the date and the discharge point where these measurements were made, and
3) geochemical and chemical kinetic rock properties (Sulfur content and Alpha values associated with the strata encountered in the minesite).

The water quality and flow data used in this study were obtained from three sources: 1) Data from samples collected at the actual field sites and analyzed by the Analytical Section of the West Virginia Geological Survey. Effluent flow measurements were made at the time of sample collection. 2) Data compiled in the Office of Surface Mining and the West Virginia Department of Energy, and 3) Information available on CRIS (Coal Reclamation Information System) DATABASE. The CRIS DATABASE includes a suite of water quality, overburden analyses, and general mine information for more than 300 minesites in the 12 northern coal producing counties of West Virginia. In addition, a complete suite of lithotypes associated with coal representing five different coal beds over a five-county area were collected and analyzed for numerous chemical properties, among which were the kinetic rate constant, alpha using a method developed and reported by the authors, and the total percent sulfur. These data are contained in a formatted form identified as the "WRI DATABASE OF CHEMICAL CHARACTERISTICS OF TOXIC ROCK MATERIALS". A compilation of the alpha value and the total percent sulfur ranges for different lithologies is shown in Tables 1 and 2 respectively.

Table 1 Range of alpha values for specific lithotypes from WRI database

TYPE	HIOH RANOE ALPNA	LOW RANOE ALPHA
BONE COAL	0.003428	0.000274
OVERBOROEN SHALE	0.009978	0.000073
PIT REPUSE	0.010681	0.001020
PREP REPUSE	0.030556	0.001074
ROOP SHALE	0.026499	0.000165
SANOSTONE	0.131424	0.000271
SEATEARTH	0.167421	0.001428
SRALE PARTING	0.105798	0.000676
SILTSTONE	0.021484	0.006730

TABLE 2. Range of sulfur values for specific lithotypas from WRI database

TYPE	LOW RANCE SOLPUR	HIGH RANOE SULPUR
BONE COAL	0.195	5.040
OVERBUROEN SHALE	0.221	9.736
PIT REFUSE	0.080	4.242
PREP REFUSE	0.032	9.572
ROOF SHALE	0.030	7.010
SANDSTONE	0.004	10.063
SEATEARTH	0.037	9.144
SHALE PARTINO	0.047	6.334
SILTSTONE	0.046	0.374

The Simulation

Following is a brief description of an actual computer simulation defining what the computer is doing and what decisions the computer is expected to make.

1. The computer reads into memory the following minesite data:
   a. The permit number
   b. Dates of active mining
   c. Present mine status
   d. Type of surface mine
   e. The disturbance acreage
2. The computer reads into memory the following field data:
   a. The date of sampling
   b. The location of sampling
   c. The sulfate concentration of the effluent
   d. The effluent flow measurement
3. The computer then determines the statistical relationship between the sulfate concentration data and the flow data for each sampling location. This is done for each season of the year. It is at this point that the computer is programmed to decide whether the sulfate-flow relationship for each discharge point and each annual season is:
   a. A completely random number (Figure 8)

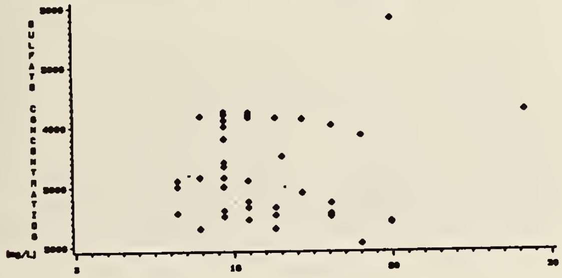

Figure 8. Random nature of sulfate concentration vs flow. Data from site DLA 71-75.

   b. A statistically significant inverse curve (Figure 9)

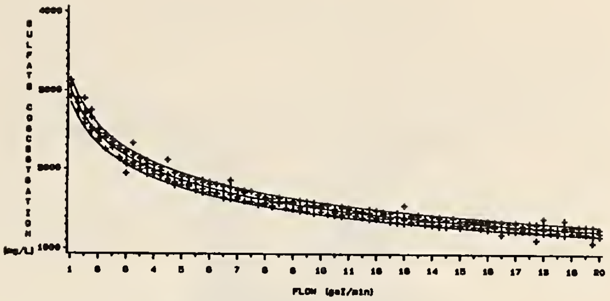

Figure 9. A computer generated statistically significant inverse relationship for sulfate concentration vs flow. No such relationship was encountered during the study.

   c. A multimodal random number (Figure 10)

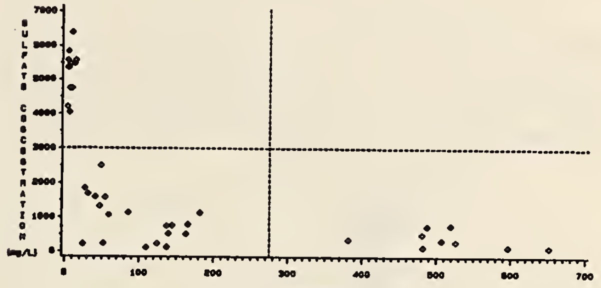

Figure 10. A multimodal random relationship between sulfate concentration vs flow. Data from site Bethel Road Refuse File.

These are the three relationships that have been shown to exist between sulfate concentration in the effluent and the flow measurement of the effluent. The criteria on which the computer makes this decision can be seen in table 3.

Table 3. Oetermination of data distribution type based on flow and sulfate concentration data.

TYPE OF OATA DISTRIBUTION	TYPE OF CORRELATION	CORRELATION COEFFICIENT	REMARKS
TOTALLY RANDOM	PEARSON	< 0.20	(SEE FIO. 8)
	40%-60% OF 10 RANDOM POINTS SNOW NEOATIVE SLOPES IN 1000 TRIALS	-----	
INVERSE	POWER TRANSPORMATION	> 0.90	(SEE PIG. 9)
MULTIMOOAL RANDOM	CANONICAL OROUP CLUSTER	------	DEFAULTS IP OTHER OISTRIBUTIONS FALL (SEE FIO. 10)

4. The computer will then read available stratigraphic information, determine the volume percent of each significant stratigraphic layer, and will then determine an operational alpha value for the minesite based upon the compilation of alpha values in the "WRI DATABASE" and the geologic cross section or drill core log.

When all of the aforementioned information has been generated, the computer enters "RANDOM SIMULATION MODE", which is the portion of the software that determines the BETA value associated with the minesite.

RESULTS AND CONCLUSIONS

Results of the Simulation

Figure 3 is a histogram of beta values generated by 1 million computer simulations and beta generations for a particular minesite. The field data for this graph are from the DLM permit 135-78 in Upshur County, WV. This distribution of beta is quite acceptable based on the narrow range of potential beta values that were generated.

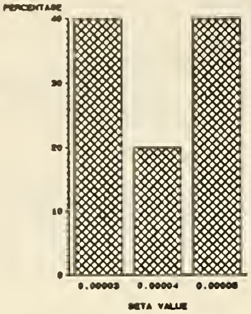

Figure 3. Histogram showing the range of beta values for site DLM 135-78 obtained from SSPE/PSM.

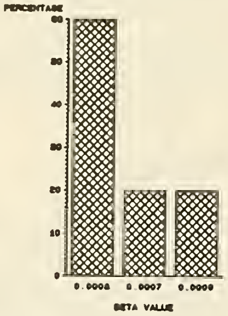

Figure 4. Histogram showing the range of beta values for site Bethel Road Refuse Pile obtained from SSPE/PSM.

Figure 4 shows a histogram for 1 million computer-generated beta values that correspond to field data on the Bethel Road gobpile, Monongalia, Co., WV. Note that the range of beta values calculated for the gobpile is smaller than the range of beta values for the DLM 135-78 site. The reason for the difference lies mainly in the characteristics of the materials of which the two sites are constituted. In a gobpile the material is essentially a single, relatively homogeneous lithology, namely prep plant refuse, while in a reclaimed surface mine, there is a diversity of lithologies. As a result, the number of combinations of possible sulfur and alpha values associated with the diverse lithologies found in a reclaimed surface mine are considerably greater than in the monolithologic gobpile.

This successful simulation was accomplished with a minimum number of empirical formulae. The simulation has completely absorbed all of the randomness associated with the measurement and distribution of these data. As can be seen in Table 4, the statistical distribution of the sulfate concentration and flow values generated in the random simulation matches the statistical distribution of the original data set very closely. In other words, the mining system has been found to adhere to the Simultaneous Species Production-Elimination principle.

Table 4. DLM 135-78 sulfate and flow, actual (field) and simulation statistics.

VARIABLE[1]	MEAN	STANDARD DEVIATION
----------------	DISCHARGE PT = 1	----------------
FIELD SULFATE	1,272.4	234.1
SIMULATION SULFATE	1,274.4	230.8
FIELD FLOW	19.7	9.8
SIMULATION FLOW	19.8	9.5
----------------	DISCHARGE PT = 2	----------------
FIELD SULFATE	2,589.7	633.3
SIMULATION SULFATE	2,587.8	638.0
FIELD FLOW	17.1	4.7
SIMULATION FLOW	17.3	4.5
----------------	DISCHARGE PT = 2A	----------------
FIELD SULFATE	2,244.1	507.7
SIMULATION SULFATE	2,238.8	504.8
FIELD FLOW	1.5	0.59
SIMULATION FLOW	1.5	0.57
----------------	DISCHARGE PT = 2B	----------------
FIELD SULFATE	2,633.1	443.5
SIMULATION SULFATE	2,599.9	448.8
FIELD FLOW	15.3	5.7
SIMULATION FLOW	15.2	5.4

[1] Sulfate measurements in mg/L and flow measurements in gal/min.

With the computer generation of a beta value, all the data needed to analyze the pyrite oxidation and oxidation product elimination associated with the system are available. Using EQUATION 2, sulfate concentrations of effluents were calculated using a time-series algorithm.

Figure 5 shows the computer-projected sulfate concentration of the minesite discharge of DLM permit 135-78. The discharge is projected to 250 mg/L sulfate concentration (drinking water standard). From this plot it is possible to make an estimate of the acid-producing lifetime of the minesite. The computer-generated curve is based on all of the sulfate and effluent discharging from a single point. Figure 6 displays a significant break that

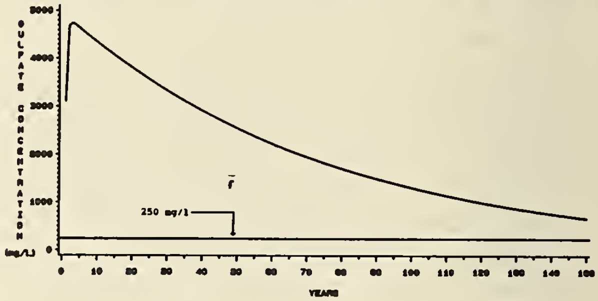

Figure 5. Curve showing the longevity for site DLM 135-78.

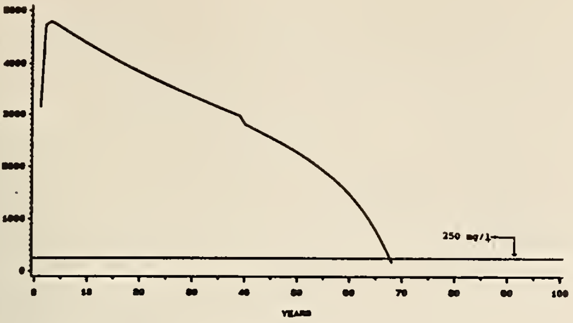

Figure 6. Longevity curve for DLM 135-78 with a 'hypothetical break' point.

occurs when alpha no longer plays a significant role in the system. It is at this point that the amount of reactive material has been reduced to a negligible level. This break point is arrived at using the laws of chemical kinetics and the mean-lifetime concept of reactive substances. This estimation is preliminary and further study is necessary to ascertain a more exact break point. Table 5 gives the beta and longevity information, the time required before the level of oxidation products released from the system is environmentally acceptable within the context of existing regulations, for the sites studied. The time (years) axis corresponds to the elapsed time from the initiation of mining.

Table 5. Beta values and projected longevities of various studied minesites.

MINE SITE	BETA (1/days)	ACTIVE LONGEVITY (years)
BETHEL ROAD GOBPILE	5×10^{-3}	30-40
DLM 135-75 MT. TOP REMOVAL	5×10^{-4}	45 +
DLM 23-76 MT. TOP REMOVAL	2×10^{-4}	45 +
DLM 71-75 MT. TOP REMOVAL	5×10^{-4}	45 +
DLM 58-77 MT. TOP REMOVAL	5×10^{-4}	45 +
EVERETTSVILLE GOBPILE	5×10^{-3}	25-30
PIERCE SITE	2×10^{-4}	50 +
WALNUT HILL GOBPILE	1.5×10^{-3}	28 +

Amelioration and the SSPE/PSM Model

The amelioration production-elimination model allows the development of an amelioration strategy. Beta values, being related to physical parameters, do not change with amelioration. Alpha, on the other hand being related to chemical parameter values do change. The purpose of amelioration is to reduce the alpha value (the rate of pyrite oxidation) to a level where the mine system will approach a condition known as 'secular equilibrium'. When a system has achieved secular equilibirum, the build-up of oxidation products is drastically reduced. At this point, the concentration of oxidation products being generated approaches zero. Figure 7 shows the theoretical effect on the sulfate concentration of a mine discharge existing at various alpha levels. The alpha and beta values chosen to generate this graph are those associated with the DLM permit 135-78. The curve is denoted as 'control'. This graph does NOT show the existing effect of amelioration on this particular minesite, but what the effect would have been had proper amelioration of pyrite oxidation been carried out as part of the overall mining operation while the minesite was active. The lowest curve represents an alpha reduction of 1000 times. The curve (alpha = 0.000008) is the upper boundary of 'secular equilibrium'. The mathematics dictate that the sulfate concentration must gradually increase, but it can be easily seen that below the curve corresponding to alpha = 0.000008, in the region of 'secular equilibrium', the concentration of pyrite oxidation products in the discharge are quite manageable. Not only are the concentrations of oxidation products being generated very low, but the build up of oxidation products in the system is also low.

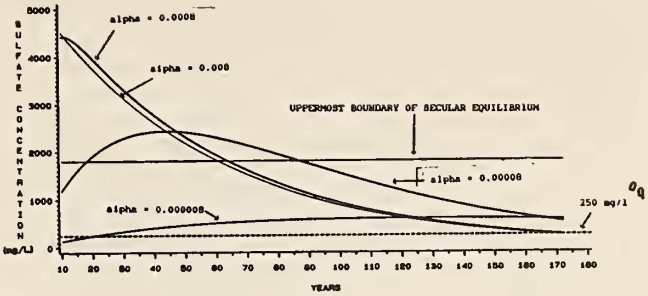

Figure 7. Effect of amelioration on the alpha value of a mining system.

Hydrological Impact Assessment and the SSPE/PSM Model

The proposed model can also be used to evaluate the hydrological impact assessment potential of a proposed minesite. Knowing the alpha, beta and discharge distribution for a particular mining operation, a discharge simulation is possible. When this discharge simulation is added to existing stream quality data and principles of mass balance, a hydrological impact simulation (assessment) is possible.

Data were extracted from the CRIS DATABASE. Search of the data base located an area where water quality and flow data existed prior to the 1982 initiation of a proposed downstream mining operation. This particular mine site was chosen for three reasons: 1) the isolated nature of the proposed site provided an excellent proving ground for the simulation, 2) the proposed site was to be a mountaintop removal operation; a mine type for which the beta (chemical elimination) constants for the pyrite-sulfate system were reasonably well established during the course of this current research endeavor, and 3) stream quality data for a downstream area were compiled in 1985. Using the pre-1982 water quality data and the available general mine information data, a new prototype model was developed for the purpose of simulating the mine discharge into the stream from a minesite exhibiting the chemical patterns reflective of the pre-1982 data. The model included the development of alpha and beta values that could be expected for species other than sulfate ion. The simulation was used to project the change in basic water quality parameters that would result from the mining operation and predict the water quality that would be seen by the year 1985. These predicted data were then compared to the actual 1985 data taken downstream from the 1982 mining operation. Using beta values found to be common to mountain top removal operations for the respective ions in question, this new prototype computer simulation package and a system now comprised of the mining operation and the receiving stream, the results shown by the 1985 water quality study were accurately projected (See table 6).

Table 6. CHIA predictive capabilities of PSM modeling technique for a selected mining operation.

CHEMICAL SPECIES	1982 ANALYSIS (mg/L)	2-YEAR PROJECTON	1985 ANALYSIS (mg/L)
SULPATE	940	slight increase to 1,020 mg/l	1,030
IRON	58	very slight increase; estimate should be (statistically) about equal	48
ACIDITY	510	moderate increase (15%)	575
MANGANESE	.05	no statistical change	.04

CONCLUSIONS

This research has established several important points: 1) the nature of the data associated with a mining operation is too randomly distributed and too high in intrinsic error of measurement to be used in a reliable empirical model. 2) the distribution of this randomness and error can be incorporated into a viable model provided this model is designed to deal with distributions of data, rather than discrete data points or statistical averages assumed to be Gaussian distributions. Such modeling technique is called a "RANDOM PROBABILITY SIMULATION" or PSM. In order to utilize a PSM one must first find a logical, scientifically sound principle that governs the system in question. The mathematical concept of Simultaneous Species Production-Elimination meets all logistical and scientific criteria as a governing principle for the generation and discharge of geochemical parameters associated with pyrite oxidation in a mining operation. 3) this mathematical principle incorporated into a PSM allows the critical evaluation of the pyrite oxidation-acid elimination relationship that exists in a mine. Knowing this relationship allows scientifically sound amelioration planning and with modification, will allow the development of a viable hydrological impact assessment procedure that will be relatively free from guesswork and random error. The relationship between pyrite oxidation and effluent discharge for a particular mining operation can be quickly established using existing field data, making the model quite useful in reclamation planning with abandoned mine lands.

ACKNOWLEGEMENTS

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CHEMICAL STABILITY OF MANGANESE AND OTHER METALS IN ACID MINE DRAINAGE SLUDGE[1]

George R. Watzlaf[2]

Abstract.--Federal regulations require mine operators to reduce the average concentration of manganese in the effluent to 2 mg/L. To meet this standard, the majority of mine operators add an alkaline material, typically lime or sodium hydroxide, to raise the pH to about 10.0. Our laboratory tests using actual acid mine drainage (AMD) containing iron, manganese, nickel, copper, zinc, and chromium, have indicated that the high-pH precipitation method is effective at removing these metals. However, manganese, nickel, zinc, and copper in the precipitated sludge were susceptible to dissolution upon subsequent depression of pH. Up to 30 percent of the original manganese in the high-pH precipitated sludge dissolved at pH 7.5. At pH 6.0, this figure increased to 78 pct. Additionally, 30 percent of nickel, zinc, and copper redissolved at pH values of 6.8, 5.7, and 4.7, respectively. Iron and chromium were stable down to pH 3.5. No differences were found between the use of lime or sodium hydroxide regarding the stability of the precipitated sludge. In mine waters containing high concentrations of iron in relation to manganese and other metals, manganese and other metals were removed at lower pH values than in mine waters with less iron. However, manganese in the sludge precipitated from the high iron water was less stable. Aging also affected the stability of manganese in AMD sludge. After sludge had aged for three months, 50 percent less manganese was released upon depression of pH. The problem of manganese redissolution can be avoided by using an oxidizer such as sodium hypochlorite or potassium permanganate; however, these chemicals were ineffective at removing copper, nickel, and zinc. To reduce manganese below 2 mg/L, the use of sodium hypochlorite or potassium permanganate increased chemical treatment costs by factors of 2.3 and 2.6, respectively, over the chemical costs for sodium hydroxide treatment.

INTRODUCTION

Chemical Treatment for Manganese Removal

Federal legislation requires mine operators to adhere to specific effluent limits (U.S. Code of Federal Regulations 1985 a & b) (table 1). To meet these limits, treatment of acid mine drainage typically involves addition of alkaline material, commonly lime (CaO or $Ca(OH)_2$) or sodium hydroxide (NaOH); natural or mechanical aeration; and settling. When the pH of the drainage is raised to 7 or 8, and there is sufficient time allowed for settling, most mine drainage water will meet the

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

[2] George R. Watzlaf is an Environmental Engineer, U.S. Bureau of Mines, Pittsburgh Research Center, Pittsburgh, PA.

Table 1.--Federal effluent limitations

Pollutant or pollutant property	Maximum for any 1 day	Average of daily values for 30 consecutive days
Iron, total *	7.0 mg/L	3.5 mg/L
Manganese, total	4.0 mg/L	2.0 mg/L
Total Suspended solids	70.0 mg/L	35.0 mg/L
pH	between 6.0 and 9.0	

*New source performance standards for total iron; daily maximum - 6.0 mg/L and 30-day average - 3.0 mg/L

standards for pH, iron, and suspended solids. However, this treatment will rarely reduce manganese levels below effluent limits because the oxidation rate of Mn^{2+} is pH-dependent and extremely slow below pH 8.5. Diem and Stumm (1984) found that dilute solutions of manganese nitrate ($Mn(NO_3)_2$), maintained at pH 8.4 in the presence of dissolved oxygen, showed virtually no oxidation for over 4 years. Owens (1963) reported that a pH of at least 9.4 was necessary to remove manganese. Our tests indicate pH values above 10 are necessary for some mine drainage waters. Therefore, to ensure adequate removal of manganese, many mine operators must add enough alkalinity to raise pH of the mine water to about 10. This increases chemical treatment costs 20 to 100 pct over the costs to remove iron (Watzlaf 1985) and generates a large volume of metalliferous sludge, up to 33 pct (by volume) of the treatment plant inflow (Holland et al. 1968). Nicholas and Foree (1979) found that increasing the treatment pH from 8 to 10 increases the required sedimentation basin area from 158 m^2 to 400 m^2 for NaOH, and from 200 m^2 to 316 m^2 for lime.

The precipitation and removal of manganese in an aqueous system is complex. Manganese can exist in oxidation states of +2, +3, +4, +6, and +7 (Sienko and Plane 1966, Morgan 1967). Initially, the valence of manganese in the air-oxidized precipitate (removed at high pH) lies between 2.67 and 3.0 (Mn_3O_4 - hausmannite and β-MnOOH - feitknechtite, respectively) (Hem 1981, Murray et al. 1985). Both these minerals are eventually transformed into the more stable γ-MnOOH - manganite (Murray et al. 1985, Stumm and Giovanoli 1976). Manganese can also be removed by adsorption onto reactive surfaces. Ferric hydroxide ($Fe(OH)_3$) and manganese precipitates can provide surfaces for sorption of Mn^{2+}, which occurs at lower pH values than necessary for manganese removal as hydroxides (Morgan and Stumm 1964, Stumm and Morgan 1981, Collins and Buol 1970). Therefore, manganese in mine waters with high iron concentrations can usually be removed at lower pH values than manganese in mine water with lower iron levels. However, manganese precipitated with iron was found to go back into solution upon acidification (Collins and Buol 1970).

Additionally, manganese can exist in many different complexed and chelated forms (Martell and Calvin 1952, Clark et al. 1977, Evangelou 1984). The formation of manganese complexes depends on oxidation state, pH, bicarbonate-carbonate-hydroxide equilibria, and the presence of other materials (Nalco Chemical Company 1979). Organic complexes can hold manganese in solution to higher pH levels (Clark et al. 1977).

As an alternative to precipitation of manganese by the high-pH method, strong oxidizers, such as permanganate, chlorine dioxide, hypochlorite, or ozone can be used. These chemicals oxidize manganese to pyrolusite (MnO_2) (Evangelou 1984, Clark et al. 1977). Knocke et al. (1987) found that hydrogen pyroxide was not effective for oxidizing manganese.

In the process of removing manganese by the high-pH precipitation method, arsenic, chromium, copper, lead, mercury, nickel, selenium, and zinc should precipitate, principally, as hydroxides (Feitkecht and Schindler 1963). These metals may also be removed by sorption onto iron precipitates (Jones 1986, Mott et al. 1987, Slavek and Pickering 1986) and as with manganese, complexes and chelates may be formed (Martell and Calvin 1952). However, hydroxides of these metals may resolubilize if solution pH is changed (Peters and Ku 1985). Bogner (1983) found that for treated mine drainage, the order of extractability from the retention pond sediments was Mn > Ni, Zn, Co, > Cu, Cr > Fe, Al. Forbes et al. (1976) reported that 50% of Cd, Zn, Pb, and Cu was desorbed at pH 8, 7, 5.5, and 5, respectively, from synthetic iron oxide (goethite).

Regulation of Manganese

During the process of developing effluent limitation guidelines for the coal mining industry, the Environmental Protection Agency (EPA) found that certain metals, such as arsenic, chromium, copper, lead, mercury, nickel, selenium, and zinc, were occasionally present in the untreated mine water. Water treatment specifically to control iron (neutralization and aeration) reduced the concentrations of these toxic metals, but not consistently enough to provide effective control as required by the Clean Water Act of 1972.

Selection of a specific manganese standard was a result of a survey of 314 acid water sources (Weideman 1982). In their survey, EPA researchers found that the mine water treatment facilities were reducing manganese to approximately 2 mg/L, and therefore selected that value as the best available technology (BAT) effluent limit (U.S. Code of Federal Regulations 1985b). In addition, the eight toxic metals of concern (arsenic, chromium, copper, lead, mercury, nickel, selenium, and zinc) were reduced to acceptable levels whenever manganese was reduced to 2 mg/L. Therefore, limitations on these metals were not promulgated. In their survey of acid mine drainage sites, the EPA found average manganese concentrations in the untreated mine water of 4.9 mg/L at underground mines and 17.7mg/L at surface mines (Weideman 1982). The highest concentration of manganese was 63 mg/L at any surveyed site. However, a decade later, our work has found many sites at which manganese levels exceed those found by the EPA. The average manganese concentration from 23 sites with known manganese problems was 121 mg/L. Twenty of these sites had manganese levels over 63 mg/L (the maximum level in the EPA survey) and three sites exceeded 200 mg/L (Kleinmann and Watzlaf 1988).

EXPERIMENTAL PROCEDURES AND RESULTS

This paper summarizes research performed over the past 3 years. In these investigations, five mine waters with different chemical compositions were used (table 2). This section is divided into three subsections: manganese removal, manganese resolubilization, and behavior of other metals. In the following subsections, several experiments are discussed; and although similar procedures were used for each test, some modifications were necessary to account for the different water quality of individual mine waters. Therefore, for clarity, the experimental procedures are following immediately by the results of that particular test.

In all tests, pH was measured with an analog meter using a combination pH electrode. Acidity analysis consisted of a fixed endpoint titration to pH 8.3 using a 1N sodium hydroxide solution. Iron, manganese, aluminum, copper, nickel, zinc, and chromium concentrations were determined by inductively coupled argon plasma (ICAP) sprectroscopy. In all tests, immediately after a sample was collected for metal analyses, it was passed through a 0.45 µm membrane filter and acidified to less than pH 1.0 with concentrated hydrochloric acid. In all tests, concentrations have been corrected for dilution of all added solutions.

Table 2.--Water quality of mine waters

Water quality parameter	Concentration of untreated AMD*				
	I	II	III	IV	V
Iron	232	51.3	7.7	7300	39
Manganese	126	87.7	84.3	76.5	44
pH	5.3	3.1	3.1	2.0	5.0
Acidity	467	535	NA	18475	NA
Copper	NA**	NA	0.27	22.6	NA
Nickel	NA	NA	2.87	15.8	NA
Zinc	NA	NA	4.59	39.1	NA
Chromium	NA	NA	<0.04	1.82	NA
Aluminum	3.8	34.9	NA	NA	NA

*All concentraions in mg/L except pH in pH units. Acidity in mg/L as $CaCO_3$.
**NA = Not Analyzed.

Manganese Removal

Mine waters I and II were used to compare the treatment costs of three chemicals that were currently being used by the mining industry to remove manganese: sodium hydroxide (NaOH), sodium hypochloride (NaOCl), and potassium permanganate ($KMnO_4$). These three chemicals represent two basic treatment options for manganese; addition of enough alkaline material (NaOH or lime) to raise pH to approximately 10 or use of a chemical oxidant (NaOCl or $KMnO_4$) for direct manganese oxidation. Chemical treatment costs were calculated using the prices of the chemicals at the time of the study (1984) and as delivered to the mine: $0.28/gal and $0.80/gal, for bulk quantities of 20-pct-NaOH and 15-pct-NaOCl solutions, respectively, and $1.34/lb for granular $KMnO_4$. Bulk purchase price of $KMnO_4$ is about $1.08/lb, but a typical mine would not require such large quantities (minimum 20 metric tons).

For mine water I, 50 liters of raw water was collected and treated with a 20-pct solution of NaOH to raise pH to 7.5. This water was then aerated by pouring it from one container to another, causing iron to oxidize and precipitate and pH to decrease. The procedure of neutralization and aeration was repeated until pH stabilized at 7.5. Analysis showed that iron was reduced to approximately 4 mg/L and manganese to 95 mg/L. Addition of alkaline material prior to addition of the chemical oxidant is common practice since much of the iron can be easily removed and since discharge pH must be above 6.0. After settling for 30 minutes, twenty 400-ml samples of the supernatent water were collected in plastic bottles. Six of these bottles received incremental amounts of additional NaOH (5-pct solution) with pH raised to between 9.2 and 10.5. Six bottles received incremental amounts of a $KMnO_4$ solution (1 pct). Seven bottles received incremental amounts of NaOCl (8 pct available chlorine) and one bottle received no extra chemical addition. After settling for 23 hours at room temperature, a sample from each bottle was filtered, acidified, and analyzed. All three treatments were capable of reducing manganese below effluent limits, but sodium hydroxide was considerably less expensive than the chemical oxidants. Total chemical costs to treat 1,000 gal of mine water I (including $0.36 for the initial NaOH) averaged $1.02, $2.30, and $2.60 for NaOH, NaOCl, and $KMnO_4$, respectively (Watzlaf 1985).

Similar tests were conducted on mine water II. A 50-liter sample of water was collected after being treated by the existing hydrated lime ($Ca(OH)_2$) treatment system. As in the above test, the mine water was manually aerated, after which the pH stabilized at 8.2. After 30 minutes of settling, iron was reduced to 2 mg/L and manganese to 70 mg/L. Based on previous lime use records, it was estimated that this treatment to pH 8.2 cost approximately $0.22 per 1000 gal of water. Twenty-seven 450-ml samples were taken from this treated water and incremental amounts of NaOH (5-pct solution), NOCl (8 pct available chlorine), or $KMnO_4$ (1-pct solution) were added to respective bottles. These bottles were mixed and left to settle for 90 minutes. Samples from each bottle were filtered, acidified, and analyzed. Total chemical costs per 1,000 gal to reduce manganese to 2 mg/L were $0.53, $0.95, and $1.70 for NaOH, NaOCl, and $KMnO_4$, respectively (Kleinmann et al. 1985).

In performing these and other tests (Ackman and Kleinmann 1985), it was observed that in the high-pH precipitation method, manganese was removed at lower pH values if the mine water contained higher concentrations of iron with respect to manganese. The next test used mine waters III and IV. Note that the iron to manganese concentration ratio in mine water III is 1:11, while in mine IV this ratio is 95:1. One liter of each mine water was stirred in a large beaker. A 5-pct solution of NaOH was incrementally added to the water. After addition each increment of NaOH, pH was measured and a 50-ml sample was taken from each beaker. Figure 1 shows the removal of iron and manganese as a function of pH. In the high iron water, manganese is removed at approximately 1.5 pH units lower than in the low iron water. Presumably, some manganese is removed during the precipitation of iron by adsorption on $Fe(OH)_3$ (Stumm and Morgan 1981).

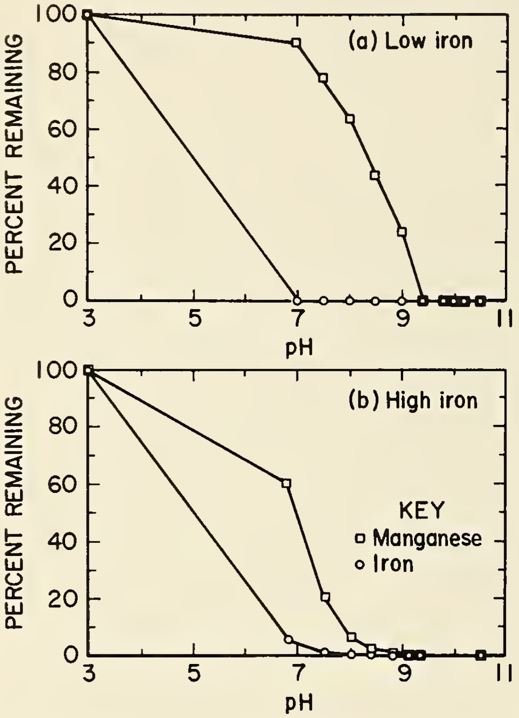

Figure 1.--Removal of iron and manganese from acid mine drainage containing (a) low (7.7 mg/L) and (b) high (7,300 mg/L) iron concentrations using the high-pH precipitation method (sodium hydroxide).

Manganese Resolubilization

From the above tests, it was observed that the high-pH precipitated manganese would resolubilized upon depression of pH. Approximately 800 ml of mine water V was placed in four beakers and slowly stirred. To the first beaker, a 5-pct solution of NaOH was added to raise pH to 10.5 to ensure complete manganese removal. To the second beaker, a hydrated lime ($Ca(OH)_2$) slurry was added to raise pH to 10.5. To the third and fourth beakers, a 5-pct-NaOH solution was added to raise pH to 7.2. The third beaker then received NaOCl treatment (2 pct available chlorine) and the fourth received a 1-pct solution of $KMnO_4$. The treated mine water was stirred for 15 minutes and 50-ml samples from each beaker were filtered and acidified. To each beaker incremental amounts of a dilute sulfuric acid (H_2SO_4) were added to lower pH. At various pH levels, 50-ml samples were taken. No differences in resolubilization of manganese were found between the two high-pH precipitation methods using lime or sodium hydroxide (figure 2). Approximately 50 pct of the precipitated manganese resolubilized after pH was lowered to 3.5. However, no manganese resolubilization of manganese occurred for the sludge precipitated with the chemical oxidants (NaOCl and $KMnO_4$).

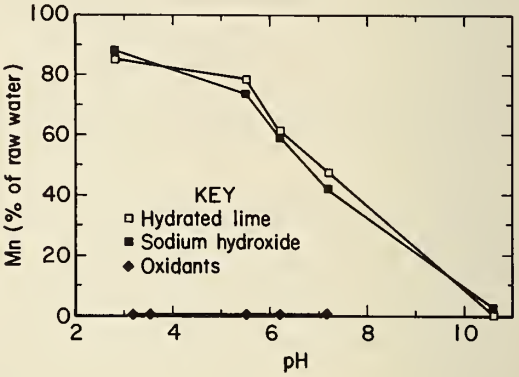

Figure 2.--Comparison of manganese resolubilization from acid mine drainage sludge precipitated with sodium hydroxide and hydrated lime (high-pH method) and with chemical oxidants (Sodium hypochlorite and potassium permanganate).

Although an elevated iron to manganese ratio facilitated manganese removal, it also resulted in a less stable sludge. Mine waters III and IV were treated with a 5-pct solution of NaOH to pH 10.5. Dilute sulfuric acid was added to each mine water and samples were taken at various pH levels as in the previous test. Figure 3 shows the removal and resolubilization of manganese for mine waters III and IV, which have iron to manganese ratios of 95:1 and 1:11, respectively. For the high-iron AMD, the removal and resolubilization curve follow the same path. Presumably, this indicates that much of the manganese was removed by adsorption to ferric hydroxide, and subsequently desorbed with depression of pH. For the low-iron water, the manganese in the sludge was more stable.

The other factor that influenced the stability of manganese in AMD sludge was the age of the sludge. Mine water V was treated with NaOH (20-pct solution) to pH 10.5 and the water-sludge mixture was stored in a loosely covered container. After aging for three months, the mixture was stirred and H_2SO_4 was added to lower the pH. Figure 4 shows that the manganese in AMD sludge becomes more stable as it ages.

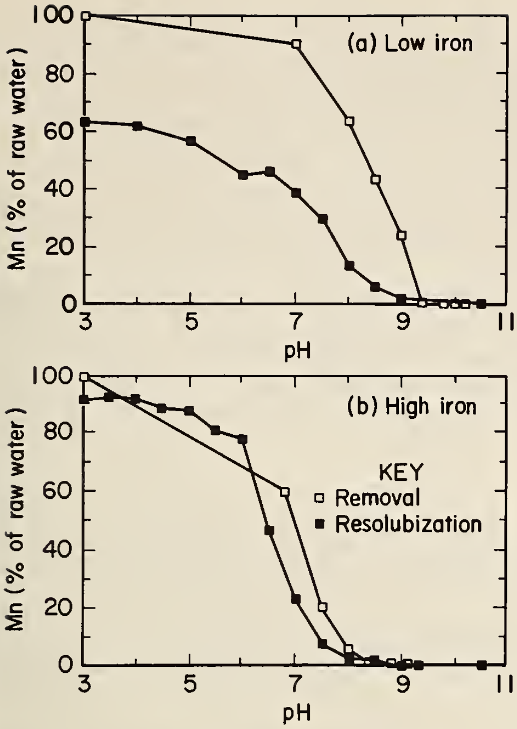

Figure 3.--Removal and resolubilization of manganese. Untreated acid mine drainage contained (a) low (7.7 mg/L) or (b) high (7,3000 mg/L) iron concentrations. Sludge was precipitated with the high-pH method using sodium hydroxide.

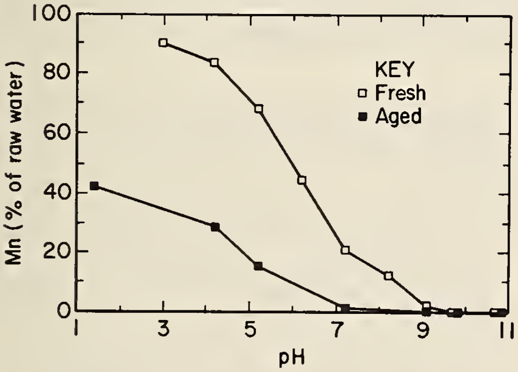

Figure 4.--Comparison of manganese resolubilization from freshly precipitated acid mine drainage sludge and sludge aged 3 months. Sludge was precipitated with the high-pH method using sodium hydroxide.

Behavior of Other Metals

Regulation of manganese was based partly on the fact that it acted as a surrogate for removal of other potentially more toxic metals. Therefore, concurrent with the test on mine waters III and IV outlined above, the removal and resolubilization of other metals were also investigated. Figure 5 shows the removal of the other metals from mine waters III and IV. The ratios of iron concentration to the sum of the concentrations of other metals (manganese, copper, nickel, zinc, and chromium) were 1:12 and 47:1 for mine waters III and IV, respectively. Like manganese, these metals were removed at lower pH values in the high-iron mine water presumably by adsorption to ferric hydroxide. The resolubilization of these metals was also influenced by the concentration of iron in the mine water (figure 6). These metals were more soluble in sludge precipitated from the high iron mine water.

We also investigated the ability to permanganate and hypochloride to remove copper, nickel, zinc and chromium. NaOH (5-pct solution) was added to 1 liter of mine water IV to raise pH to 6.0 and was left to settle for 3 days. This partially neutralized, water-sludge mixture was split into three equal portions and sampled. One portion was treated with a 5-pct-NaOH solution to pH 10.4, another portion was treated with a 1.5-pct solution of potassium permanganate, and the remaining portion treated with an 8-pct available chlorine solution of hypochlorite. Analyses showed that the initial neutralization to pH 6.0 removed all of the chromium and some of the nickel, zinc, copper and manganese. Treatment with NaOH removed the remaining amounts of these metals. However, the oxidants, while effectively removing manganese, were unable to remove nickel, zinc, or copper.

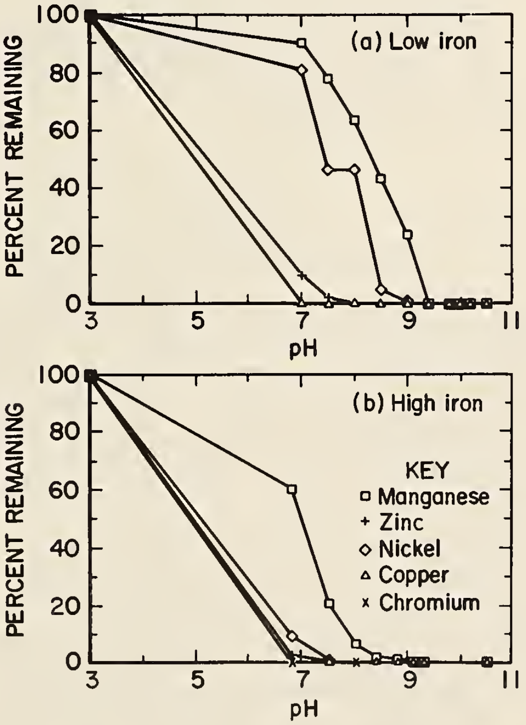

Figure 5.--pH required to remove manganese, zinc, nickel, copper, and chromium from acid mine drainage containing (a) low (7.7 mg/L) and (b) high (7,300 mg/L) iron concentrations using the high-pH precipitation method (sodium hydroxide).

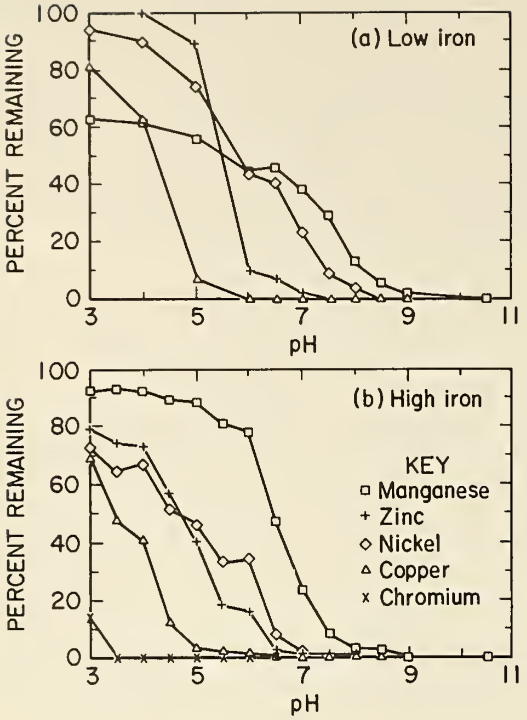

Figure 6.--Resolubilization of manganese, zinc, nickel, copper, and chromium from sludge precipitated from acid mine drainage containing (a) low (7.7 mg/L) and (b) high (7,300 mg/L) iron concentrations. Sludge was precipitated with the high-pH method using sodium hydroxide.

DISCUSSION

In order to comply with effluent limits for manganese, mine operators have two main treatment options: use of alkaline materials for high-pH removal or use of chemical oxidants. The principal advantage of the high-pH method is cost. Chemical costs for this method are two to three times less than for the chemical oxidants. However, at some sites, the reduction of manganese to 2 mg/L may necessitate discharging water with a pH higher than the effluent limit of 9.0. A mine operator in this situation is commonly granted a variance that permits a high-pH discharge, which may be deleterious to the environment (Kleinmann and Watzlaf 1986). Another disadvantage of the high-pH method is the instability of the sludge it produces. Although we found that the manganese in the sludge becomes somewhat more stable after three months, up to 30 percent can resolubilize at pH 4.2. The effects of longer aging periods are not known. If the sludge is disposed of in or on the backfill, any manganese that resolubilizes may need to be retreated. The same may be true of underground disposal. This cycle of treatment, precipitation, sludge disposal, resolubilization, and retreatment may be repeated indefinitely at great expense to the operator. In fact, the high manganese concentrations currently found in some mine drainage may be due to sludge resolubilization.

The use of chemical oxidants produces a stable manganese precipitate, however, treatment costs are greatly increased. These chemicals also require very accurate control of dose rate. In order for hypochlorite to be effective, enough chemical must be added to produce a chlorine residual. With adequate detention time and proper chemical dosage, this chlorine residual will dissipate before discharge. However, overtreatment and pond short-circuiting could result in discharge of high residual chlorine levels and damage to the environment. Similarly, the dosage of permanganate needs precise control. Too much permanganate will result in excess MnO_4^-, which will place the effluent in violation of the manganese limit. Also, although very effective at removing manganese, these chemicals do not remove nickel, zinc, or copper.

The problem of resolubilization of manganese and other metals from acid mine drainage sludge is potentially very significant. Millions of tons of AMD sludge have been and are being disposed of with little or no concern to potential metal resolubilization. The resolubilization of this sludge could cause mining companies significant increases in treatment costs or, if released to the environment, substantial environmental damage. Additional research is needed to determine the effects of long-term aging on AMD sludge in the treatment pond and after disposal. Other factors involved in removal and resolubilization need to be delineated in order to evaluate current treatment and disposal practices.

CONCLUSIONS

Tests using five different mine waters investigated the removal and resolubilization of manganese as well as other metals from AMD using various chemical techniques. The major conclusions of this study are:

1. When sodium hydroxide or lime was used, minimum pH values necessary to reduce manganese below 2.0 mg/L ranged from 8.4 to 10.2.

2. The pH necessary to remove manganese from mine water with an iron:manganese ratio of 95:1 was approximately 1.5 pH units less than from a mine water with an iron:manganese ratio of 1:11.

3. In the high-iron mine water (7,300 mg/L), 50% of manganese, nickel, zinc, and copper resolubilized at pH 6.6, 5.8, 5.6, and 3.5, respectively.

4. In the low-iron mine water (7.7 mg/L), 50% of manganese, nickel, zinc, and copper resolubilized at pH 5.6, 4.5, 4.7, and 4.3, respectively.

5. Manganese was stable to pH 3.5 in the sludges generated with permanganate or hypochlorite.

6. The high-pH method using sodium hydroxide significantly reduced concentrations of nickel, zinc, and copper; however, permanganate and hypochlorite did not.

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TREATMENTS TO COMBAT PYRITE OXIDATION IN COAL MINE SPOIL

C.A. Backes, I.D. Pulford, and H.J. Duncan[1]

Abstract. Oxidation of pyrite and its inhibition by various waste materials were studied using pyritic spoil from Central Scotland, with the aim of developing procedures to prevent reacidification after the initial treatment. It had previously been shown that the rate of pyrite oxidation could be decreased by complexing or precipitating the iron species involved. Analysis of leachate from a set of lysimeters showed that the rate of pyrite oxidation increased with the onset of warmer weather, but was greatly reduced during winter. A controlled temperature incubation experiment investigated the inhibition of pyrite oxidation by chicken manure or conifer bark at 0, 8, 18 and 30°C. There was no significant pyrite oxidation in the limed spoil. In the unlimed spoil more oxidation occurred at 18 and 30°C than at 0 and 8°C. Conifer bark reduced the rate of pyrite oxidation at all temperatures, and at 18°C it reduced it to that found at the lower temperatures. Chicken manure completely inhibited acid and iron production at all temperatures. A small field trial investigated the use of chicken manure, conifer bark, sewage sludge, and oil shale waste in conjunction with lime to inhibit the rate of pyrite oxidation. The plots were seeded with grass, and vegetation yield and spoil characteristics measured. These plots are being continued, to study the long-term effects of the amendments on pyrite oxidation.

INTRODUCTION

Pyrite is present in many of the colliery spoil heaps (bings) in Central Scotland, and is the major obstacle to their reclamation. Acidic spoil, resulting from the oxidation of the pyrite, is traditionally neutralised by the addition of lime. However, after a few years bings suffer from acid regeneration, as the lime is leached out and more pyrite oxidises. The reacidification tends to occur in localised areas as the distribution of pyrite in a bing is seldom homogeneous (Backes 1984). These acidified areas tend to spread, killing any established vegetation.

Many bings receive only the initial reclamation treatment and, even when large quantities of lime are added in an attempt to account for potential acidity, either in one or a number of applications, the bings still tend to suffer from acid regeneration. Doubleday (1974), for example, found that four applications of limestone totalling 100 t/ha over a two-year period were inadequate to neutralise the acidity of one spoil; Costigan et al. (1981) found spoils limed at either 50 or 100 t/ha which reacidified after one or two years. Some bings do receive aftercare,

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especially if they are to be used for agricultural purposes. In these cases it may be possible to apply additional lime to small areas of the bing as they reacidify, to neutralise the acid and inhibit the spread of pyrite oxidation. However, it would be preferable if there were one initial treatment, which not only neutralised the acid already present in the bing, but also prevented further reacidification of the spoil. This paper proposes such treatments.

There are two main pathways for pyrite oxidation, either using oxygen or ferric ions as the oxidising agent. Above about pH 4.5 oxidiation will only occur by the oxygen pathway. This is a relatively slow process and does not produce large quantities of acid. However, if the pH falls to below 4.5 then ferric ions act as an oxidising agent on pyrite. The ferric ions are produced by the bacterially catalysed oxidation of ferrous ions, which are liberated from the pyrite. This leads to a cyclic system, in which ferrous ions are bacterially oxidised to ferric ions, which are then reduced by their action on pyrite back to ferrous, simultaneously releasing more ferrous ions from the pyrite. This is a much faster reaction than oxidation by oxygen, leading to a rapid release and build-up of acid. Backes, Pulford and Duncan (1986, 1987) showed that the ferric ion oxidation pathway could be inhibited by the use of specific chemicals to interfere with the cycling of iron. Phosphates and silicates were used to precipitate the iron, whilst citrates were used to complex it. Use of a bactericide stopped the production of ferric ions by the action of Thiobacillus ferrooxidans. These studies, which were carried out in suspensions of pyritic coal waste, showed that the treatments restricted the oxidation pathway to that by oxygen alone, so decreasing the rate at which acid was released. Waste materials were also used to inhibit the oxidation of pyrite by ferric ions. Chicken manure and chopped conifer bark both complexed the iron, while pulverised fuel ash (a source of silicate) precipitated it. The work reported here extends these laboratory studies on waste materials into controlled pot and field studies.

METHODS

Pyritic spoil was obtained from Baads Colliery, West Lothian (Ordinance Survey of Great Britain ref NT 002609), and all field work was conducted on this site. The pyritic content of the spoil had been previously measured as ranging from 0.07 to 2.92%, using the method of Dacey and Colbourn (1979). However, lumps of pyritic material could easily be found in the field which contained up to 75% FeS_2. The heterogeneity of pyritic spoil has been discussed by Backes (1984). Baads bing was originally reclaimed in 1979, when the lime requirement was 25 t/ha to account for existing acidity plus 25 t/ha for potential acidity. Large areas of the bing have since suffered from severe acid regeneration.

Field Lysimeters

A series of lysimeters was set up in the field in February 1987, five containing pyritic spoil and two with nonpyritic spoil as the controls. Each lysimeter had a volume of $0.01m^3$ and was imbedded into the surrounding spoil. The leachate was collected weekly and filtered through Whatman's No. 1 filter paper. It was analysed for pH, titratable acidity by titration with sodium hydroxide to phenolphthalein end point, and total soluble iron by atomic absorption spectrophotometry. The weekly rainfall, and maximum and minimum air temperatures were also noted. Any rain which had not penetrated the spoil was discarded (this occurred only after very heavy rainfall).

Controlled Temperature Incubation Study

Bags of pyritic spoil, previously air-dried and sieved through a 4 mm sieve, were placed at four different temperatures; 0, 8, 18 and 30°C. After a few days, when the spoil had equilibrated, it was used to prepare a series of pots for each temperature. To four replicate pots of 500 g spoil, the following were added: no addition (control); 15 g lime (equivalent to 15 t/ha, the nominal lime requirement); 60 g chopped conifer bark (60 t/ha); 50 g chicken manure (50 t/ha); conifer bark plus lime at the above rates; chicken manure plus lime at the above rates. The spoil and amendment were thoroughly mixed before being placed in a pot. All sets of pots were returned to their original temperature and watered regularly to maintain them at near field capacity. At intervals, all the pots were leached with 100 cm^3 distilled water, and the leachate filtered and analysed as for the lysimeter study.

Field Study

Small plots (2 m by 2 m) were prepared on the area of the bing that had suffered the most severe acid regeneration, where all the vegetation had been destroyed. All plots, apart from the controls, were treated with lime at 15 t/ha and one of the following: chicken manure at 25 t/ha, sewage sludge at 20 t/ha, conifer bark at 60 t/ha, conifer bark at 30 t/ha, oil shale waste at 50 t/ha. One plot was left as lime only. The amendments were incorporated into the top 15 cm of spoil. All treatments were replicated three times in a randomised block design. The area was then fertilised (300 kg/ha of 15:10:10 NPK compound fertilizer) and seeded with an agricultural grass mix (100 kg/ha). The plots were sown in August 1986, and at the beginning of the next spring they were refertilized. The grass was harvested in 1987, and its yield measured. The spoil of each plot was sampled in duplicate and analysed for pH (1:2.5 spoil:water) and water-extractable iron.

RESULTS AND DISCUSSION

Lysimeter Study

The rate of acid and iron production in the lysimeter study reflected the rate of pyrite oxidation (figs 1, 2). The cumulative rate was obtained by multiplying the weekly rainfall by the concentration of acid or iron and then summing over the appropriate weeks. Although the spoil for all the pyritic lysimeters was obtained from a small area, the quantity of acid and iron produced varied considerably, reflecting the heterogeneity of the pyritic content of the spoil. Initially the rate of oxidation was very slow, but between weeks 14 and 16 (at the end of May) the rate increased dramatically. The limits of the change of rate were shown in lysimeters 1 and 5; the rate of acid production per lysimeter changed from 7 μg H$^+$ per week to 136 μg H$^+$ per week in lysimeter 1 and from 11 to 60 μg H$^+$ per week in lysimeter 5. The rate of iron production changed from 75 μg Fe per week to 1900 μg Fe per week for lysimeter 1 and from 54 μg Fe to 500 μg Fe per week in lysimeter 5. This increase in rate occurred in all the lysimeters (apart from the controls) over the same two-week period; the rate then stayed approximately constant for each lysimeter until week 32, when the rate decreased in all lysimeters. This increase and decrease in rate closely corresponded to the measured air temperature (fig 3). At week 16, the weekly minimum temperature began to rise above 0°C, whereas the maximum temperature had begun to rise about week 9. The rate of acid production would probably correlate most closely to the average temperature, rather than the maximum or minimum. The approximately constant rate after week 16 would suggest that there was a rate limiting mechanism operating during the summer period. The solubility constant (Ksp(Fe)(OH)$_3$) for ferric hydroxide ranges from 4 x 10^{-38} to 2.7 x 10^{-39}, depending on which form of hydroxide precipitates. During the summer period the leachate was supersaturated with respect to these oxides, suggesting that one of these forms was controlling the concentration of iron in solution, and thus limiting the rate of pyrite oxidation. Other iron compounds can precipitate, such as jarosite and a large number of intermediate iron products, whose solubility would be greater than that of the hydroxides. It would depend on the exact local conditions as to which iron compound precipitated (Nordstrom 1982). In the colder period, the leachate was supersaturated with respect to the stable iron oxides, but not so with respect to the more amorphous oxides. As it would be expected that the amorphous oxides would precipitate in this situation, it seems

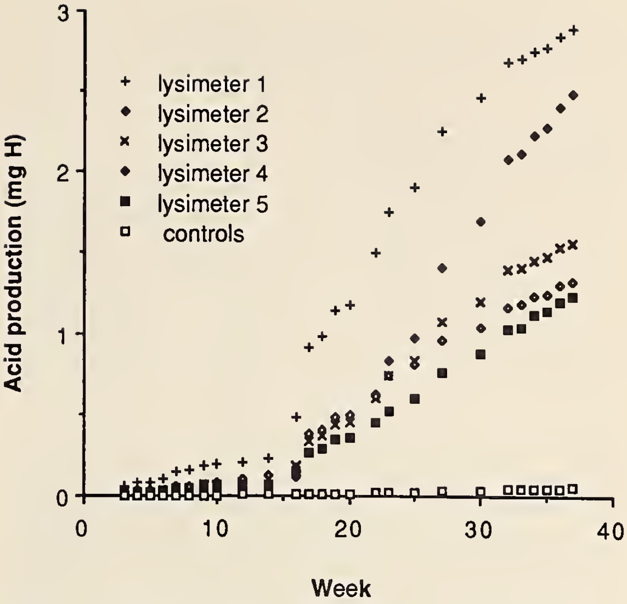

Fig 1. Cumulative acid production in lysimeters.

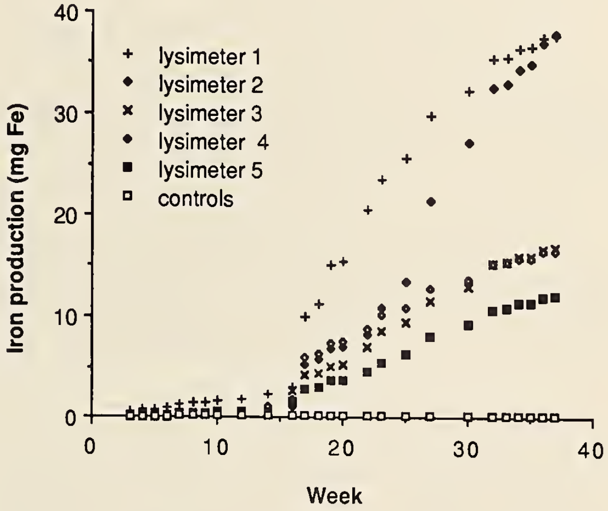

Fig 2. Cumulative iron production in lysimeters.

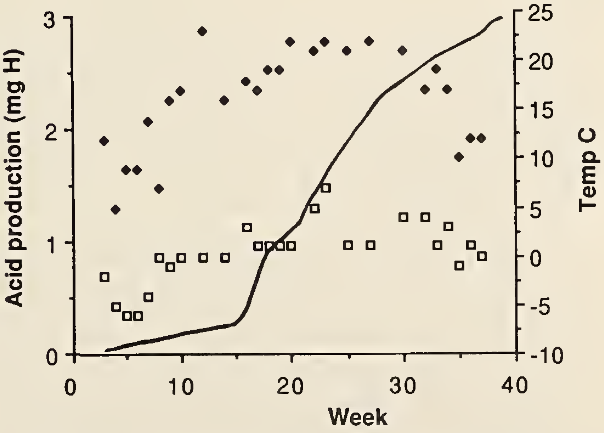

Fig 3. Relationship of acid production to air temperature (lysimeter 1, maximum T, minimum T).

that in the cold period precipitation of ferric ions was not occurring and thus not rate limiting. Apart from the precipitation of an iron hydroxide, there are three other factors which can limit the rate of pyrite oxidation by ferric ions in the field. The rate limiting step in the oxidation pathway can be either the bacterial oxidation of ferrous to ferric ions, or the actual ferric ion oxidation of pyrite, or the surface area of the pyrite available for reaction with the ferric ions (Garrels and Thompson 1960, Bloomfield 1972, van Breemen 1973). As the rate of oxidation was much greater in the summer period than in the colder period, it would suggest that the last two mechanisms would not be rate limiting in the colder period, otherwise they would have decreased the summer rate. However, it is very probable that the rate of ferrous ion oxidation by Thiobacillus ferrooxidans was decreased due to the fall in temperature, or it is possible that this process was completely absent, restricting the oxidation of the pyrite to that by oxygen alone, which is a much slower process.

Controlled Temperature Incubation Study

The limed pots at all temperatures maintained a pH above 5.5. This high pH would restrict the rate of pyrite oxidation to that by oxygen alone, and therefore no conclusions can yet be drawn as to the effect of amendment and lime on the rate of pyrite oxidation from this study.

In the unlimed pots the rate of pyrite oxidation varied with temperature, although for the first 40 days, it was nearly the same at all temperatures. After this the rate of acid production was approxiamtely 16 µg H^+ per day at 18 and 30°C and 6 µg H^+ per day at 0 and 8°C (fig 4). The rate of iron production was 10 µg Fe per day at 0 and 8°C, 40 µg Fe per day at 30°C, and 70 µg Fe per day at 18°C. (Only results for acid production are presented graphically as the overall trends were the same for acid and iron). This was not such a marked difference in rate between temperatures as had occurred in the lysimeter study.

The conifer bark reduced the rate of pyrite oxidation at all temperatures, and at 18°C it reduced it to the rate at the lower temperatures (figs 5, 6, 7). The chicken manure completely inhibited the rate of acid and iron production at all temperatures (figs 6, 7, 8).

After day 155, the pots at 0 and 8°C were moved to 8 and 18°C respectively to simulate the rise in temperature occurring in the field. The pots at 18°C were not moved as it is only rarely that the spoil would maintain a temperature above this in the field in Scotland. The pots at 30°C were indicative of the maximum acid and iron production, although more iron was actually produced in the 18°C pots (lime-only pots). There was no discernible change in the rate of pyrite oxidation in the 0 and 8°C pots when the temperature was raised to 8 and 18°C respectively.

Conifer bark and chicken manure both complex iron (Backes 1984, Vaughan, Wheatley and Ord 1984), either by chelating it on to the solid material or by forming a stable complex in solution. Both these amendments decreased the rate of pyrite oxidation at all temperatures, presumably by complexing the iron and inhibiting the ferric ion oxidation of pyrite. The amendments could have been complexing the products of the pyrite oxidation, reducing the measurable amounts of acid and iron, leading to the false conclusion that the actual rate of oxidation was decreased. However, in view of the lysimeter results, it would seem that at least at the higher temperatures they were actually inhibiting the ferric ion oxidation of pyrite.

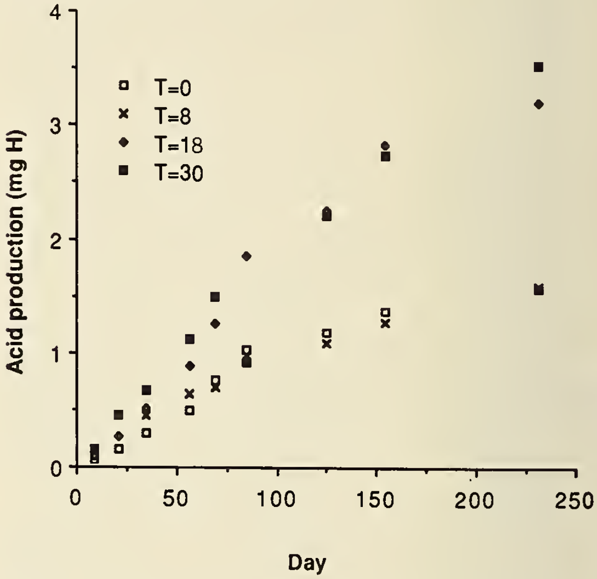

Fig. 4 Cumulative acid production in control pots at all temperatures.

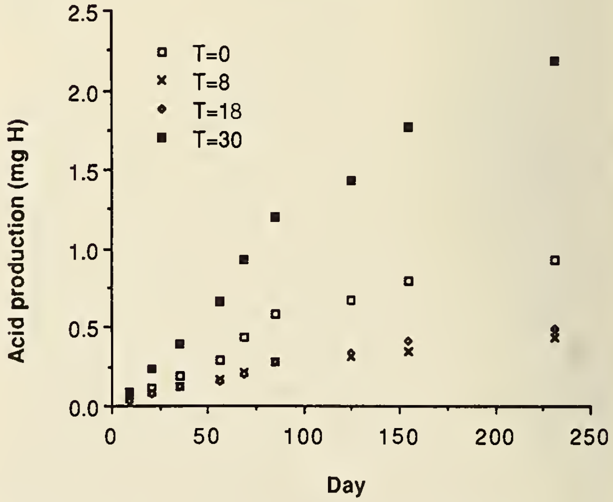

Fig. 5 Cumulative acid production in pots amended with conifer bark at all temperatures.

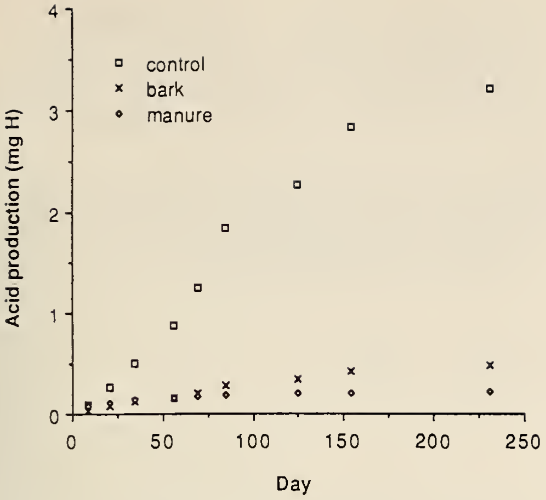

Fig. 6 Cumulative acid production in unlimed pots at 18°C.

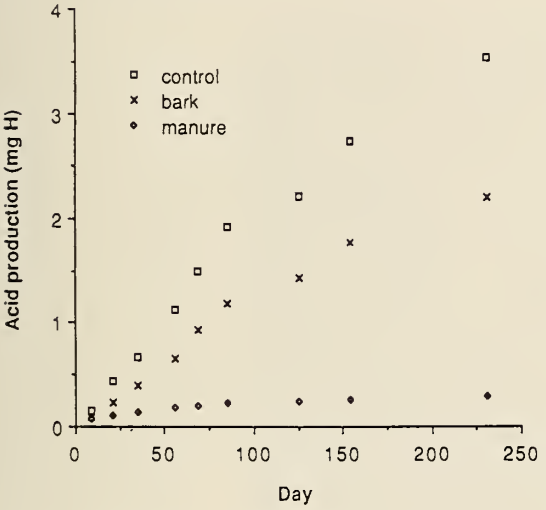

Fig 7. Cumulative acid production in unlimed pots at 30°C.

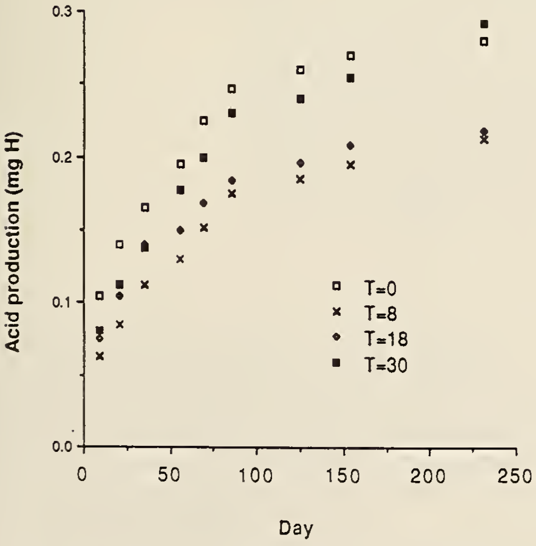

Fig 8. Cumulative acid production in pots amended with chicken manure at all temperatures.

Table 1 : Vegetation yields on limed plots amended with various organic treatments, 1 year after establishment.

Treatment	Mean yield of vegetation (and s.d.) (g/m^2)
Chicken manure	374 (87)
60 t/ha conifer bark	321 (105)
Sewage sludge	320 (114)
30 t/ha conifer bark	286 (99)
Lime only	262 (56)
Oil shale	233 (28)

Field Study

After one year the pH of spoil in all the plots, apart from the unamended controls, was above 6.5. There was a large variance in the yields from each treatment, which means that statistically the differences in yields were not significant (table 1). However, the general trend was that all the amended plots, except for those treated with oil shale, gave greater yields than those treated with lime alone. In the case of the sewage sludge and chicken manure plots, this may have been due to an added nutrient effect, but this would not be the case for the conifer bark plots. Therefore there was probably some beneficial effect occurring in terms of inhibition of pyrite oxidation. The oil shale waste was rather an inert material, and may require attack by acid before it releases silica. This field trial is being continued, so that when the added lime has been neutralised or leached out the effectiveness of the amendments at inhibiting pyrite oxidation in the field can be measured.

CONCLUSIONS

The preliminary results of this study point to ways of inhibiting the reacidification of colliery spoil. Any of these amendments would have to be added to an acidic bing in conjunction with lime, by incorporation into the plough layer, as otherwise the pH would be too low to allow for the establishment of vegetation.
This would lead initially to the oxidation of pyrite being inhibited due to the high pH, as ferric hydroxide would precipitate and Thiobacillus ferrooxidans would be inoperative. In time the effect of the lime would be reduced, as the slow rate of pyrite oxidation produced acid which would neutralise the lime, and as lime was leached out of the spoil. The amendments would then start to be effective, by complexing any iron that came into solution, thus restricting the oxidation of pyrite to that by oxygen alone. This should prevent the rapid reacidification of the spoil, allowing a vegetation cover to be established, which itself would act as a source of organic matter for the spoil.
A continual supply of organic matter to the spoil would ensure that once the original amendment had been completely degraded

there would still be an iron complexing source available. The build-up of a vegetation cover would also restrict the infiltration of air into the spoil, thus decreasing the rate of pyrite oxidation further. If the amendments are added in the colder period of the year, it may help to ensure that all iron produced is immediately complexed, thus precluding the onset of rapid reacidification of the spoil.

ACKNOWLEDGEMENTS

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A GROWTH INHIBITION MODEL FOR THIOBACILLUS FERROOXIDANS[1]

Kay L. Shuttleworth and Richard F. Unz[2]

Abstract.-- Acidophilic strains of the genus *Thiobacillus* play a major role in the genesis of acidic mine drainage. The development of these chemolithotrophs has been shown to be adversely affected by the presence of certain organic acids in laboratory cultures. Conversely, acidophilic heterotrophic bacteria, e.g., members of the genus *Acidiphilium*, are capable of metabolizing a variety of organic acids. A theoretical model was developed which mathematically depicts a possible interaction between these two physiologically distinct types of microorganisms. The model is based on the Monod kinetics model modified to account for the effects of exogenous inhibitors on the chemolithotroph when co-cultured with the heterotroph. Application of the model assumes that the two types of bacteria can coexist in a chemostat receiving two different limiting nutrients, one for each microorganism. For purposes of illustrating the model, (a) growth of the chemolithotroph and the heterotroph are assumed to be limited by ferrous iron and an organic acid, respectively, and (b) the organic acid is inhibitory to the chemolithotroph. In addition, the predictive value of the model is dependent on the assumptions that there is no product inhibition and the level of ferrous iron is not inhibitory to the heterotroph. In this model, the steady state biomass of *T. ferrooxidans* is a function of the maximum growth rates and substrate half-saturation constants of both members of the population as well as the inhibitor constant of the chemolithotroph. The model indicates that the growth of *T. ferrooxidans* may be strongly linked to the growth of other organism(s) capable of removing organic inhibitors.

INTRODUCTION

The microbial aspects of acidic mine drainage have been the subject of many investigations (Dugan 1975, Harrison 1978, Wichlacz and Unz 1981). One of the key reactions in the formation of acidic mine drainage is mediated by the chemolithotrophic, iron-oxidizing bacterium,

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Thiobacillus ferrooxidans. This organism obtains energy from the oxidation of ferrous iron or reduced sulfur compounds and sustains the oxidation of pyritic sulfur by providing a continuous supply of the oxidant, Fe^{+3} (Singer and Stumm 1970). Furthermore, hydrolysis of the ferric iron yields the mineral acid, H_2SO_4, which is responsible for the low pH of the drainage.

T. ferrooxidans and other acidophilic thiobacilli are of economic importance because of their role in the genesis and continued production of acidic mine drainage; therefore, many researchers have studied the effects of inhibitors on the thiobacilli (Borichewski 1967, Tuttle and Dugan 1976, Tuttle et al. 1977). Compounds which have been found to inhibit the acidophilic thiobacilli include pyruvate, acetate, succinate, glutamate, and fumarate. In addition, there has been much interest in the inhibitory effects of a detergent, sodium lauryl sulfate (Dugan 1987, Dugan and Apel 1983, Onysko et al. 1984). A proposed scheme for the prevention of acidic mine drainage involves treating coal refuse with sodium lauryl sulfate to inhibit the thiobacilli and thus curtail the production of pollutants which characterize acidic mine waters.

The focus of most of the acidic mine drainage literature has been on the acidophilic thiobacilli; however, acidophilic heterotrophs, e.g., members of the genus Acidiphilium, have recently been isolated from acid-mineral environments (Harrison 1981, Wichlacz et al. 1986). Furthermore, nonacidophilic heterotrophic organisms may be found in gelatinous streamers in acidic mine drainage (Johnson et al. 1979).

The organic carbon utilized by heterotrophs may include compounds that are potentially toxic to the acidophilic thiobacilli. It has been shown that acidophilic heterotrophs can use succinate, glutamate, citrate, fumarate, and other similar carbon sources (Wichlacz et al. 1986), some of which have been shown also to inhibit T. thiooxidans, T. ferrooxidans, or both. Thus a potential exists for the two populations to interact in the environment through one common intermediate.

MODEL DEVELOPMENT

A. Background

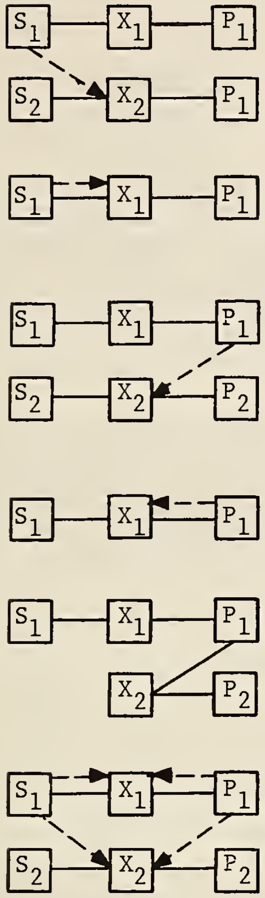
Microorganisms may be inhibited by various compounds, including microbial waste products, high concentrations of substrate, and exogenously supplied chemicals. Ways in which inhibitors can interact with two different species are shown schematically in figure 1. It is possible to develop mathematical models which describe these phenomena, and many investigators have used such models to characterize the effects of product and substrate inhibition on microbial growth (Davison and Stephanopoulos 1986, Luong 1987). Models have been developed which describe how product inhibition can be relieved by the presence of a second organism which removes that product. However, there are apparently few models which describe possible interactions between two species when one of the species is affected by an inhibitor which is not a product of the system.

In this paper, a model will be developed to express the potential interactions between two species of acidophilic bacteria, a chemolithotroph and a heterotroph, cocultured in a continuous culture system. There is no competition for a limiting substrate; however, the chemolithotrophic organism, T. ferrooxidans, is the subject of inhibition by an exogenously supplied organic acid which the heterotrophic organism, an Acidiphilium sp., can degrade. The model may predict potential interactions between the chemolithotroph and the heterotroph in an acidic drainage where exogenous inhibitors are present.

B. Assumptions

Given that T. ferrooxidans is an obligate chemolithotroph and that the Acidiphilium sp. is an acidophilic, obligate heterotroph, it is possible to coculture the organisms in the chemostat by using different growth limiting nutrients for each organism. The specific assumptions are:

(1) The growth limiting nutrient for T. ferrooxidans and for the heterotroph will be ferrous iron and an organic acid, respectively.
(2) Growth of T. ferrooxidans will be inhibited by the organic acid.
(3) The iron concentration necessary for the growth of T. ferrooxidans will not be inhibitory to the acidophilic heterotroph (Wichlacz 1980).
(4) There is no product inhibition for either organism.
(5) Given that the mechanism for inhibition of T. ferrooxidans by organic acids appears to be membrane leakage (Tuttle et al 1977), the model will account for an inhibitor which affects both the K_m and u_{max}. This is equivalent to the noncompetitive inhibition model in enzyme kinetics.
(6) The dilution rate for the chemostat is set at a rate which will allow the two species to coexist.



A. Organisms inhibited by substrate of other species.

B. Organisms inhibited by high levels of their own substrate (substrate inhibition).

C. Organisms inhibited by product of other species

D. Organisms inhibited by their own products (product inhibition).

E. Organism 2 uses product of organism 1, i.e., $P_1 = S_2$

F. All possible inhibitory effects.

Figure 1. Schematic of some possible interactions between two species with two substrates and two products. Symbols: substrate 1 (S_1); species 1 (X_1); product 1 (P_1); substrate 2 (S_2); species 2 (X_2); product 2 (P_2); positive effect (————); inhibitory effect (-------).

C. Mathematical symbols

c (subscript)	Chemolithotrophic organism (*T. ferrooxidans*)
D	Dilution rate (hr^{-1})
h (subscript)	Heterotrophic organism (*Acidiphilium* sp.)
I	Concentration of inhibitor (moles/l)
K_i	Inhibitor constant corresponding to the dissociation constant of the enzyme-inhibitor complex, moles/l (Michal 1978)
K_m	Half-saturation constant, i.e., substrate concentration when growth rate is equal to ½ maximum rate (moles/l)
L	Loss term, a function of yield (g/g)
M	Biomass concentration (g/l)
S	Substrate concentration in the chemostat (moles/l)
S_o	Substrate concentration in the feed (moles/l)
u	Specific growth rate (hr^{-1})
u_{max}	Maximum specific growth rate (hr^{-1})

D. The Model

The basis for model development will be the Monod model of bacterial growth in a chemostat (Tempest 1970). The Monod model is an equation for saturation kinetics which describes the growth of microbes in terms of a limiting nutrient and factors (K_m and

u_{max}) which are a function of the physiology of the organisms. The chemostat mimics a simplified natural environment with continuous and equal flow rates to and from the system.

In order to interpret data from mixed culture work, it is first necessary to determine the kinetic parameters (K_m and u_{max}) of the organisms in pure culture. Similarily, the K_i for the chemolithotroph must be determined from pure culture studies on T. ferrooxidans in the presence and absence of the exogenous inhibitor. When the continuous culture system is at steady state, there is no net increase in biomass; hence u = D and the relationship of specific growth rate to the other parameters for the system can be expressed for the chemolithotroph and the heterotroph in equations (1) and (2), respectively.

$$(1) \quad u_c = D = \frac{u_{maxc} * S}{K_{ms} + S} - L_c$$

$$(2) \quad u_h = D = \frac{u_{maxh} * I}{K_{mi} + I} - L_h$$

It is necessary to modify equation (1) to include the effects of a noncompetitive inhibitor. In a Lineweaver-Burke linearization of saturation kinetics, it is easy to distinguish the effects of an inhibitor by the apparent K_m and u_{max}. When these inhibitor effects are accounted for and the equation is rearranged into standard form, the result is equation (3).

$$(3) \quad u = \frac{u_{max} * S}{(K_m + S)\ (1 + I/K_i)}$$

This equation is easily derived and has been credited to Haldane who apparently first described it in 1930 (Luong 1987) and to Aiba and Shoda (Davison and Stephanopoulos 1986). The accuracy of the completed model will be highly dependent on the ability of equation (3) to predict the effects of the inhibitor. It should be noted that Luong (1987) believes equation (3) fails to adequately predict inhibitor effects when the inhibitor and the substrate are the same compound. However, this equation served as the basis for the model of Davison and Stephanopoulos (1986) for product inhibition. Furthermore, the inhibitor of T. ferrooxidans is not an available substrate for the organism.

Equation (3) must be corrected to include loss of cellular material due to cell maintenance. Again steady state will be assumed; therefore, the behavior of an axenic culture of the inhibited chemolithotroph may be described by equation (4)

$$(4) \quad u_c = D = \frac{u_{maxc} * S}{(K_{ms} + S)\ (1 + I/K_i)} - L_c$$

Thus in axenic culture, growth of the chemolithotroph will be affected by the concentration of inhibitor and the inhibitor constant. In mixed culture, the concentration of inhibitor will be determined in turn by the K_{mi} and the u_{maxh} of the heterotroph as well as the dilution rate.

The limiting substrate for the heterotroph is I and the level of limiting substrate at steady state can be determined by setting equation (5) equal to zero and solving for I. The results of this transformation are given in equation (6).

$$(5) \quad \frac{dM}{dt} = \frac{u_{maxh} * I * M}{K_{mi} + I} - L_h M - DM_h$$

$$(6) \quad I = \frac{K_{mi}\ (D + L_h)}{u_{maxh} - (D + L_h)}$$

Substituting equation (6) into (4) yields equation (7) which shows the relationship between the chemolithotroph and the heterotroph.

As stated above, the model given in equation (7) includes the simplifying assumption that (I) is not inhibitory to the heterotroph at any concentration. However, acidophilic heterotrophs can be inhibited by high levels of organics (Harrison 1981). Luong (1987) has suggested that equation (8) represents a good model for substrate inhibition. S_m is the maximum substrate level which does not cause inhibition and n is determined empirically. In order to use this model, one would have to solve equation (8) for S and substitute this back into equation (4) as given above. However, solving equation (8) for S by setting dM/dt = 0 is complicated and beyond the scope of this paper. Hence, the model developed here is appropriate only when $I \leq S_m$. This appears to be reasonable since the levels of organics in acidic mine drainage are typically very low (0.003%; Johnson et al. 1979) and the high levels (> 0.5%) of organics referred to by Harrison (1981) are typical for culture media used in conventional microbiology.

It is of interest to learn how the inhibitor affects the steady state population of the chemolithotroph. This requires that equation (9) be set equal to

$$(7)\quad u_c = \left(\frac{u_{maxc} * S}{(K_{ms} + S)\left[1 + \dfrac{K_{mi}\,(D + L_h)}{K_i \left\langle u_{maxh} - (D + L_h)\right\rangle}\right]} \right) - L_c - D$$

$$(8)\quad \frac{dM}{M * dt} = \frac{u_{max} * S}{K_m + S}\,(1 - S/S_m)^n$$

$$(9)\quad \frac{dM_c}{dt} = \frac{u_{maxc} * M_c * S}{(K_{ms} + S)\ (1 + I/K_i)} - (D + L_c)M_c$$

$$(10)\quad S = \frac{K_{ms}(D + L_c)\ (1 + I/K_i)}{u_{maxc} - (D + L_c)\ (1 + I/K_i)}$$

$$(11)\quad M_c = \frac{D\ (S_o - S)}{(D + L_c)}$$

$$(12)\quad M_c = \frac{D * S_o}{(D + L_c)} - \frac{D}{(D + L_c)} * \frac{K_{ms}\ \left[(D + L_c)\ (1 + I/K_i)\right]}{u_{maxc} - \left[(D + L_c)\ (1 + I/K_i)\right]}$$

$$(13)\quad M_c = \frac{D * S_o}{(D + L_c)} - \frac{D}{(D + L_c)} * (X) \text{ where X equals:}$$

$$\frac{K_{ms}\ \left[(D + L_c)\ \left\langle K_i \left[u_{maxh} - (D + L_h)\right] + K_{mi}(D + L_h)\right\rangle\right]}{u_{maxc} - \left[(D + L_c)\ \left\langle K_i\ \left[u_{maxh} - (D + L_h)\right] + K_{mi}(D + L_h)\right\rangle\right]}$$

zero. When equation (9) is solved for S, the result is equation (10). The steady state biomass is a function of the dilution rate, maintenance loss, initial substrate level, and the steady state substrate level and can be expressed by equation (11). Substituting equation (10) into equation (11) gives equation (12) which shows the relationship between the inhibitor level, the inhibitor constant, and the steady state biomass. However, (I) is again determined by the population of the heterotroph as given in equation (6). Therefore, equation (6) should be substituted for the value of (I) in equation (12). This results in equation (13) which could be simplified by combining terms and renaming them by definition. However, in its present form one can see that the steady state biomass of the chemolithotroph depends on the following physiological characteristics of the two microbes; the maximum growth rate of both the chemolithotroph and the heterotroph, the half saturation constants of both the chemolithotroph and the heterotroph, and the inhibitor constant of the chemolithotroph. In contrast, the steady state biomass of the heterotroph would depend only on the u_{max} and K_m for the heterotroph itself. Biomass of both the heterotroph and the chemolithotroph would, however, also depend on the yields and dilution rate.

SUMMARY AND CONCLUSIONS

A mathematical model was developed to express the potential relationship between the chemolithotroph, T. ferrooxidans, and a heterotroph, Acidiphilium sp., in the presence of a compound which inhibits T. ferrooxidans but is the growth substrate for the heterotroph. In the model, the growth of the chemolithotroph was strongly linked to the growth of the heterotroph. The model must now be verified by actual trials with the chemostat. If the model does not fit the data, the model must be altered. The key assumptions which may need to be changed are: (1) there is no substrate inhibition of the heterotroph, (2) the mechanism of inhibition of the chemolithotroph is noncompetitive, (3) there is no product inhibition, and (4) no other interactions exist between the two species.

Although the extent of inhibitory effects of organics on T. ferrooxidans in the natural environment is not known, Dispirito et al. (1981) have reported that a soluble component of pyrite was capable of inhibiting the growth of T. ferrooxidans. Furthermore, it has already been established that obligate heterotrophs or mixotrophic thiobacilli capable of growing in an acidic environment can reduce the inhibitory effects of organics on T. ferrooxidans (Harrison 1984, Nerkar et al. 1977, Unz and Wichlacz 1982).

This model should also be generally applicable to situations where one organism metabolizes or transforms a substance which is inhibitory to a second organism. There are many such cases in the microbial world, including the ability of Beggiatoa to detoxify (oxidize) H_2S (Atlas and Bartha 1987) and the ability of chlorophenol-degrading bacteria to detoxify the environment for other microbes and for higher organisms (Steiert and Crawford 1985).

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REHABILITATION OF WASTE ROCK DUMPS AT THE RUM JUNGLE MINE SITE[1]

John W. Bennett, John R. Harries and A. Ian M. Ritchie[2]

Abstract. --The release of acid, copper, manganese and zinc was a major environmental problem at the abandoned Rum Jungle mine site in the Northern Territory, Australia. The main sources of pollution were the three waste rock dumps and the heap leach pile, all containing pyritic material. The site was rehabilitated between 1982 and 1986 and, as part of this program, the dumps were reshaped and covered with a three-layer cover, including a compacted clay layer. A monitoring program has been carried out to assess the effectiveness of the works on two of the dumps. Lysimeters installed in the dumps have shown that less than 5 % of the incident rain percolates through the covers. The distribution of heat production in the dumps has been derived from measured temperature distributions and shows that the rate of pyritic oxidation was greatly reduced by emplacement of the covers. Comparison of oxygen concentrations in the two dumps before and after rehabilitation shows that the covers have greatly reduced the transport of oxygen into the dumps and effectively stopped thermal convection.

INTRODUCTION

There are many surface mine sites where acid drainage and the release of heavy metals create a major environmental problem which can continue long after mine operations cease. The problems of acid drainage occur at many mine sites around the world. There is an urgent need to know the effectiveness of techniques for controlling the release of these pollutants. At present there is inadequate knowledge and experience to allow the advantages, disadvantages and costs of various rehabilitation techniques to be compared.

Opencut mining to extract uranium/copper ore was carried out at the Rum Jungle mine in the Northern Territory, Australia, between 1954 and 1964, and the site was abandoned in 1971. However acid, copper, manganese and zinc continued to be released into the local river system (Northern Territory Department of Mines and Energy, NTDME 1987). The climate at the site is tropical with most of the 1.5 m annual rainfall occurring in the wet season from December to March.

The main sources of pollution were the three waste rock dumps and an abandoned heap leach pile, all containing pyritic material which oxidised in the presence of oxygen and water to produce sulfuric acid and heavy metal salts. These pollutants were leached by rainwater percolating down through the dumps and carried by groundwater to the river. Other sources of pollution were three opencuts, two filled with polluted water and one largely filled with tailings. The site was rehabilitated between 1982 and 1986. This paper discusses the results from monitoring two of the dumps (White's and Intermediate) and compares conditions before and after rehabilitation. Gibson and Pantelis (1988 , elsewhere in these proceedings) describe the groundwater monitoring being carried out at the site.

Probe holes were drilled down to the original ground surface in White's and Intermediate dumps (fig. 1) to provide access for measuring temperature, gas composition and water content. Three types of liner have been used. Type "n" holes (six on White's and two on Intermediate dumps) are lined with a 50 mm i.d. polyethylene pipe and sealed at the bottom to exclude water. Type "g" holes have gas ports inset into the liner at depths of 0.5, 1.0, 1.5, 2.0, 3.0, 5.0 m and then at 2.5 m intervals to the bottom of the hole. Type "p" holes have pairs of gas sampling tubes attached to the outside of the polyethylene liner to directly sample the gas in gravel-filled zones at each meter down the hole.

The first drilling program was in 1976 when six n-holes were installed in White's dump. In 1982 three g-holes were

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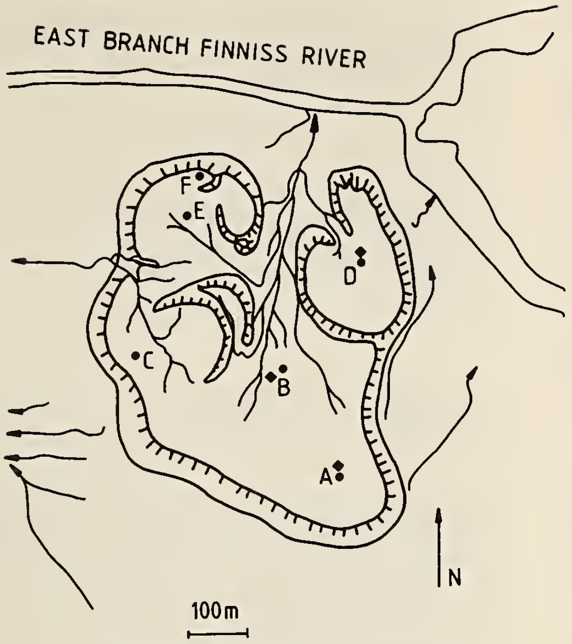
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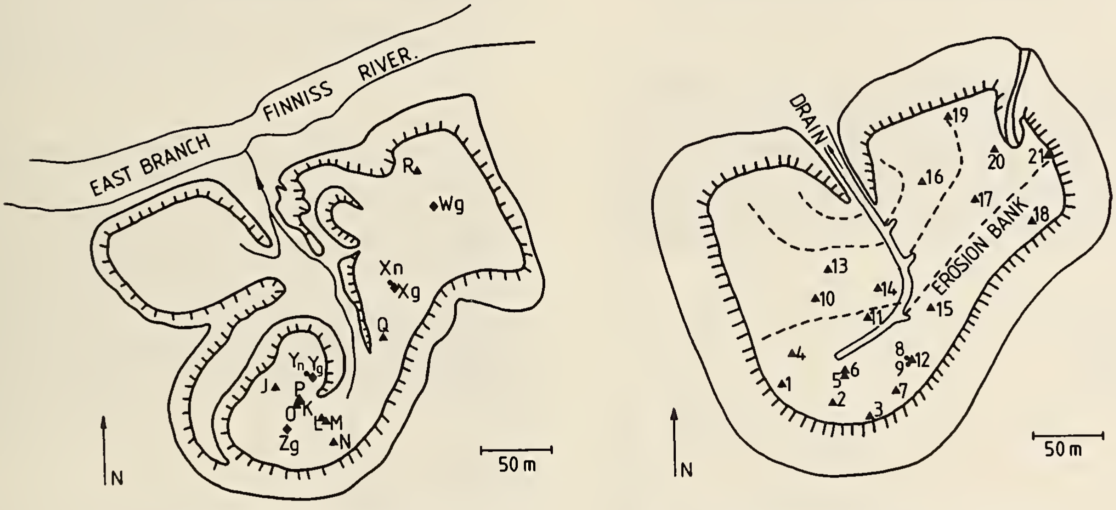
White's dump before rehabilitation.

White's dump after rehabilitation.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12
7
N
50 m

Intermediate dump before rehabilitation.

Intermediate dump after rehabilitation.

Figure 1. --White's and Intermediate dumps showing positions of probe holes before and after rehabilitation. The n-holes are shown as circles, the g-holes as diamonds, and the p-holes as triangles.

installed in White's dump. The hole in White's dumps were preserved during the earthworks which took place on White's between August 1983 and June 1984, although the length of the liners of most holes had to be adjusted to conform with the recontoured dump. Finally ten p-holes were installed in White's dump in June 1987 (fig. 1).

The first drilling program on Intermediate dump was in 1982 when four g- and two n-holes were installed. In 1984, nine p-holes were installed in Intermediate dump to provide more information on temperature and pore gas composition profiles before rehabilitation. All the holes in Intermediate dump were lost when Intermediate was rehabilitated between August and December 1985. Nineteen new p-holes were installed in Intermediate dump in November and December 1985 after the earthworks on the dump were completed (fig. 1).

REHABILITATION

The Rum Jungle site was rehabilitated between 1983 and 1986 to reduce the level of pollutants in the river, reduce public health hazards, reduce pollution levels in the flooded open cuts, and achieve aesthetic improvements including revegetation (NTDME 1987). The total cost was $(Aust)18.6 million of which $2.8 million was spent rehabilitating the three waste rock dumps (in June 1986 $(Aust)1.00 = $(US)0.68). The areas of White's, Intermediate and Dyson's dumps before rehabilitation were 26, 6.9 and 8.4 ha respectively.

The treatment applied to the waste rock dumps was designed to reduce the ingress of water and the release of pollutants. First the dumps were reshaped so that the tops had a maximum slope of 5° and and the sides a maximum slope of 1 in 3 horizontal. The tops were then covered with a three-layer cover consisting of a layer of compacted clay (minimum thickness 225 mm) on the bottom as a moisture barrier, a layer of sandy clay loam (minimum thickness 250 mm) as a moisture retention zone to support vegetation and prevent the clay layer drying out, and a layer of gravelly sand (minimum thickness 150 mm) on the top to provide erosion protection and act as a pore breaking zone to restrict moisture loss by evaporation in the dry season. A similar three-layer cover was emplaced on the sides of the dumps, but the layers were thicker (minimum thickness 300 mm of compacted clay and minimum thickness 300 mm of sandy clay loam) and crushed rock was used for the erosion barrier (minimum thickness 150 mm). Engineered runoff channels and erosion control banks were constructed on the tops and sides of the dumps. Vegetation was established to stabilise the dump surface against the long-term effects of erosion.

HEAT PRODUCTION

The oxidation of pyrite to sulfuric acid and ferrous sulfate is exothermic and releases 1440 kJ $mol^{-1} FeS_2$. It is unlikely that there are other reactions occurring which release significant amounts of heat. The released heat causes elevated temperatures in the regions where pyritic oxidation is occurring. Before rehabilitation, the temperatures at some locations within the dumps exceeded 50°C. A one-dimensional heat transfer model has been used to derive the distribution of heat production in the dumps from vertical temperature profiles measured before and after rehabilitation (Harries and Ritchie 1980, 1987). The rate of oxidation of pyrite can be obtained directly from the heat source distribution using the heat of reaction.

Before rehabilitation, heat production was occurring in White's dump at depth in holes A, C, D and F (fig. 2). After rehabilitation, the heat production was either very low or zero in all holes, with the possible exception of hole C. Comparison of heat production distributions before and after rehabilitation shows that the oxidation occurring before rehabilitation was effectively stopped by rehabilitation.

PORE GAS COMPOSITION

Before rehabilitation, the supply of oxygen was the main process limiting the rate of oxidation in the Rum Jungle waste rock dumps. The oxygen profiles showed that oxygen was transported to the oxidation sites by a combination of diffusion, thermal convection, and advection driven by variations in atmospheric pressure (Harries and Ritchie 1985). Each of these oxygen transport processes leads to a characteristic oxygen concentration profile. Thermal convection causes the oxygen concentration to be higher near the base of the dump. Diffusion causes the oxygen concentration to decrease monotonically with depth. Advection driven by variations in the atmospheric pressure leads to short-term changes in the oxygen concentration over timescales of less than a day. Increasing pressure causes air to flow into the pore space and, because the incoming air has a higher oxygen content than air already in the dump, the

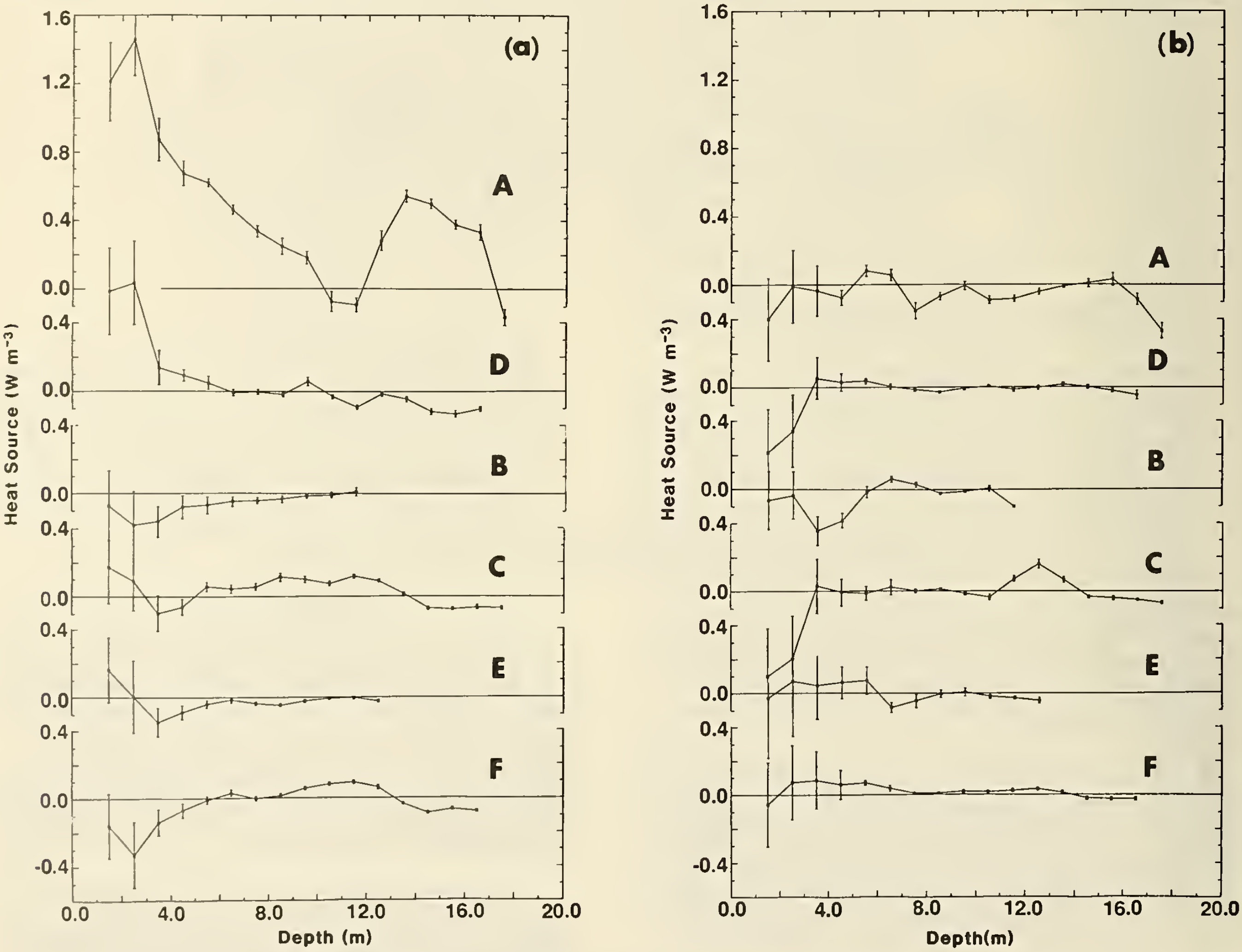

Figure 2. --Heat sources profiles derived from temperature profiles measured in White's dump (a) before rehabilitation (Mar 1979 - Sep 1983), (b) after rehabilitation (Dec 1984 - Sept 1986).

oxygen concentration measured at a given point increases. At tropical locations like Rum Jungle, the dominant atmospheric pressure variations are atmospheric tides which have two maxima and two minima a day. This causes the oxygen concentration at a given point in the dump to have two maxima and two minima a day.

Carbon dioxide concentrations measured in the dumps tended to be anticorrelated with the oxygen concentrations. This suggests that the controlling process was the rate of exchange between the interstitial gas and the atmosphere; the lower the exchange rate between the interstitial gas and the atmosphere the greater the time for the oxygen to be used in the oxidation process and the smaller the opportunity for carbon dioxide to escape into the atmosphere.

The air permeability in the rehabilitated Intermediate dump is high near the surface, lower at mid-depth, and increases at some locations near the base.

The oxygen concentration in the pore gas decreased soon after the installation of the compacted clay cover. Figures 3 and 4 show the distribution of oxygen in Intermediate and White's dumps before and after rehabilitation. The tongue of oxygenated air evident at depth in both dumps before rehabilitation indicates that thermal convection was transporting oxygen from the sides of the dumps and up through the hot regions. Since rehabilitation, the oxygen concentrations have been low at depth at all measuring points except in the northwest corner of White's dump where there are very low levels of pyrite. The clay cover effectively stopped oxygen transport by thermal convection, and greatly reduced diffusion and atmospheric pressure-driven advection.

However, after the covers had been in place for about a year, the oxygen concentrations in the top few meters were found to increase in the morning and evenings in the wet season (fig. 5). This behavior is characteristic of advection driven by variations in atmospheric pressure. The fact that these elevated oxygen concentrations were only present in the wet season can be explained by considering the effect of seasonal changes in the permeability of the compacted clay cover on the transport of air into the dump both near and away from the holes. If the clay near the holes was not as well compacted as the clay further from the holes, airflow caused by variations in the atmospheric pressure would tend to be concentrated in the higher permeability material near the holes.

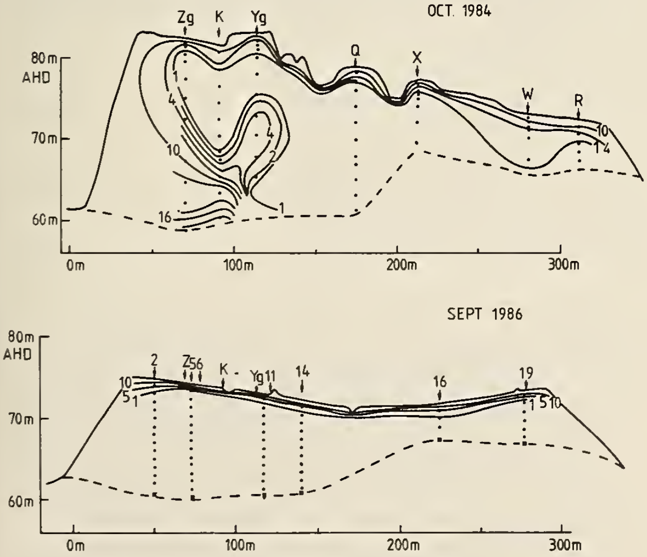

Figure 3. --Oxygen distributions in Intermediate dump (a) Oct 1984 before and (b) Sept 1986 after rehabilitation.

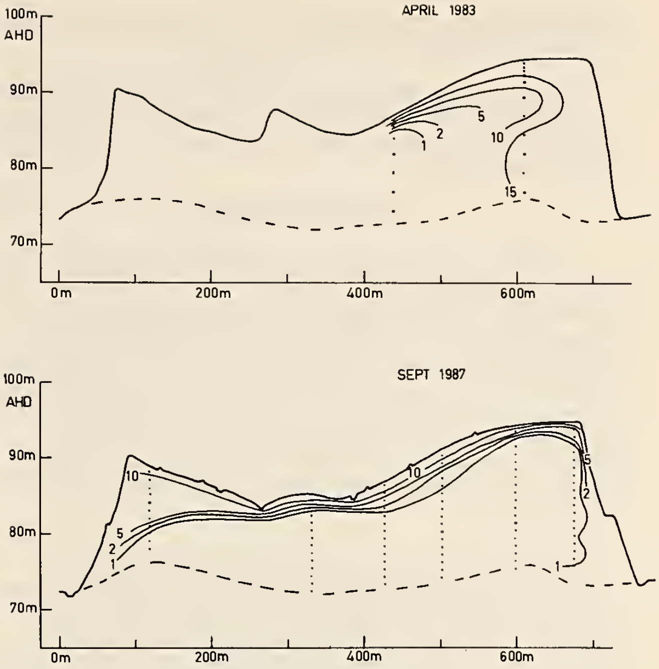

Figure 4. --Oxygen distributions in White's dump (a) Apr 1983 before and (b) Sept 1987 after rehabilitation.

The low oxygen concentrations and the lack of diurnal variation in the dry season indicate that the clay near the holes has a similar permeability to that of the clay further away. This suggests that there is cracking of the clay layer in the dry season, and that the cracks provide paths over the whole surface for advection of air by atmospheric pressure variations. The reappearance of the diurnal variations in the oxygen concentrations early in the wet season shows that most of the cracks close

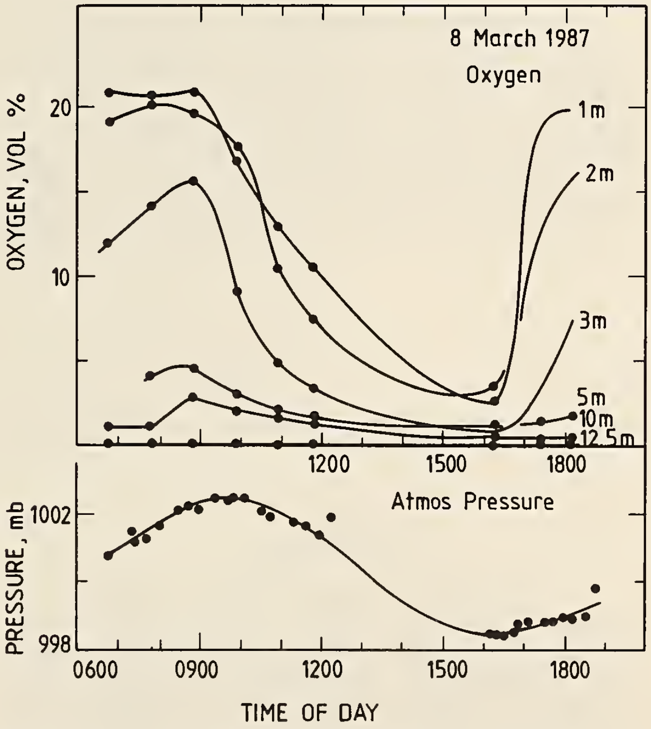

Figure 5. --Diurnal changes in the oxygen concentrations at various depths in Hole 2 in Intermediate dump during the wet season.

as the moisture content of the clay increases, but the clay near the holes does not seal as well as that further away.

Oxygen concentrations at depth in the dumps continue to be much less than they were before rehabilitation. The compacted clay cover does appear to have stopped oxygen transport by thermal convection.

WATER BALANCE

The main aim of covering the dumps was to reduce ingress of water and thereby reduce the release of pollutants. Sets of lysimeters were installed in the reshaped White's and Intermediate dumps before emplacement of the clay layer. The lysimeters consist of 200 L drums with pipes to allow any water collected to be extracted and measured. The drums are filled to 300 mm with gravel to make a water collection zone and the rest of the space is filled with dump material. Theoretical models of unsaturated waterflow have been used to verify the effectiveness of the lysimeters in collecting infiltrating water (Gibson 1987).

The amount of water collected by the ten lysimeters in White's dump in each of the three wet seasons between 1985 and 1987 is equivalent to between 2.0 and 2.5% of the incident rain. Lysimeters in Intermediate dump have only been operational for one wet season and the amount of water collected corresponds to 4.8 % of the incident rain. Before rehabilitation it was estimated that about 50% of the incident rain percolated through the dumps. These results indicate that the compacted clay cover is achieving the desired reduction in water ingress.

CONCLUSIONS

Monitoring the waste rock dumps at Rum Jungle has shown that rehabilitation by reshaping and covering with compacted clay has been effective in greatly reducing the ingress of water, the rate of oxidation of pyrite and the transport of oxygen. Further monitoring will be necessary to check that the reduction in pollution generation and water infiltration rates continue in the longer term.

The monitoring program on the waste rock dumps has allowed a quantitative assessment to be made of the effectiveness of the techniques used to reduce pollution loads from dumps. A more complete quantitative assessment will be possible when the effects of rehabilitation on ground and surface waters have been determined. However, it was recognised that improvements in the quality of ground and surface water at the mine site could take some years (Pantelis 1987, Gibson and Pantelis 1988). The lysimeters and gas composition measurements on White's dump in particular were seen as a means of acquiring early evidence of any gross shortcomings in the rehabilitation strategy which would allow the strategy to be applied to the other dumps to be modified if necessary. The reduced ingress of water and the low or zero oxidation rate (pollution generation rate) gives confidence that the release of pollutants from the waste rock dumps has decreased.

Monitoring was considered to be an important part of the Rum Jungle rehabilitation project and it was costed as part of the project. As well as the program on the waste rock dumps described in this paper, there are monitoring programs on groundwater, surface waters and vegetation. The results from all these programs will allow the cost-effectiveness of the Rum Jungle rehabilitation project to be assessed and used as a benchmark for other projects to rehabilitate mine sites where there are pyritic wastes.

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CHEMICAL INHIBITION OF IRON-OXIDIZING BACTERIA IN WASTE ROCK AND SULFIDE TAILINGS AND EFFECT ON WATER QUALITY[1]

George R. Watzlaf[2]

Abstract.--The effectiveness of sodium lauryl sulfate (SLS), potassium benzoate, and potassium sorbate in controlling the population of iron-oxidizing bacteria, thereby reducing acid production, was tested on sulfide tailings and waste rock, common waste products of metal mining. The waste rock was unweathered and contained 4.07 percent total sulfur, all in the pyritic form. Two different samples of sulfide tailings were used, an extensively weathered material (5.98 percent total sulfur, 0.17 percent pyritic sulfur, and 5.81 percent sulfate sulfur) and a slightly weathered material (20.57 percent total sulfur, 19.73 percent pyritic sulfur, and 0.84 percent sulfate sulfur). Two sample sizes were used in the experiment, 7 kg and 100 kg. The 100-kg samples of each material were treated once with a 600-mg/kg dose of SLS or potassium benzoate. The 7-kg samples were treated with a high (600 mg/kg) or low (60 mg/kg) dose of SLS, potassium benzoate, or potassium sorbate. The treated samples and untreated control samples were subsequently leached once per week with filtered demineralized water (an amount equivalent to 2.5 cm of precipitation). For the 100-kg samples of the waste rock, a single treatment of SLS and potassium benzoate completely inhibited iron-oxidizing bacteria repopulation for 182 and 231 days, respectively. Acidity in the leachate from the 100-kg samples treated with SLS and benzoate remained below the untreated control for 287 and 343 days, respectively. Similar results were obtained from the 7-kg samples of waste rock. In the extensively weathered sulfide tailings, none of the treatments inhibited the iron-oxidizing bacteria or reduced acidity levels in the leachate. In the slightly weathered sulfide tailings, all treatments reduced the bacterial populations, but did not significantly reduce acid production. However, in additional tests of the slightly weathered tailings, the removal of the weathered products prior to treatment with SLS or benzoate resulted in lower populations of iron-oxidizing bacteria and reduced acidity levels.

INTRODUCTION

The U.S. Bureau of Mines is currently researching at-source control of acid mine drainage (AMD). AMD is formed by water and oxygen reacting with the sulfide minerals that are associated with coal and metal mining wastes. A common remedy to AMD is chemical treatment of the contaminated water with alkaline materials such as lime, limestone, sodium hydroxide, or sodium carbonate. These treatments raise pH, reduce acidity, and precipitate metals. However, chemical neutralization is expensive, may be necessary for many years, and generates large volumes of sludge.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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A more direct approach is to stop or slow sulfide mineral oxidation and consequent water contamination. The chemical reactions involved in the formation of AMD can be summarized as follows:

$$2FeS_2 + 7O_2 + 2H_2O \rightleftharpoons 2Fe^{2+} + 4SO_4^{2-} + 4H^+, \quad (1)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightleftharpoons 4Fe^{3+} + 2H_2O, \quad (2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightleftharpoons 15Fe^{2+} + 2SO_4^{2-} + 16H^+. \quad (3)$$

The sulfide moiety of pyrite (FeS_2) can be oxidized by oxygen (Eq. 1) resulting in ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and acid (H^+). Ferrous iron can then be oxidized to ferric iron (Fe^{3+}), which can directly oxidize pyrite (Eq. 3). This results in additional ferrous iron, sulfate, and acid. The rate-limiting step of FeS_2 oxidation is equation 2, which proceeds slowly at low pH in the absence of iron-oxidizing bacteria such as *Thiobacillus ferrooxidans* (Singer and Stumm 1970). These bacteria, which are indigenous to areas where pyrite occurs, can accelerate the rate of equation 2 as much as 1×10^6 times (Singer and Stumm 1970). The catalytic activity of these bacteria may be the cause of over 80 pct of the AMD problem in the United States (Browning 1970).

Various chemicals can be used to inhibit *T. ferrooxidans*. Sodium lauryl sulfate (SLS) and other surfactants have been shown to reduce AMD in laboratory-scale, pilot-scale and full-scale field tests on coal refuse (cf. Stancel 1982, Kleinmann and Erickson 1982). A disadvantage of applying surfactants in solution form is the necessity to intermittently repeat the application. However, even with their short effective duration and need to reapply every three to six months, anionic surfactants can be more cost effective than treatment of the original highly acidic water with conventional alkaline materials. To remedy the need to reapply the surfactant, Kleinmann et al. (1980) developed a method using surfactant-impregnated rubber pellets that slowly release a surfactant over a longer period of time.

In an attempt to identify chemicals that have a longer effect when added as solutions, organic acids and their ability to form sparingly-soluble salts were studied (Onysko et al. 1984a). It was hypothesized that these salts would precipitate on pyrite surfaces and that these precipitates would dissolve upon decrease in pH to the biologically active form. This scheme was intended to extend the inhibitory effects of these chemicals. Salts of benzoic acid and sorbic acid were deemed appropriate for study (Onysko et al. 1984b). In laboratory and pilot-scale tests on coal refuse, benzoate and sorbate were found to be effective bacterial inhibitors; however, no increase in duration of effective inhibition was noted relative to conventional SLS solution application (ibid).

Potassium benzoate and potassium sorbate at low concentrations should have no adverse effects on the aquatic environment. These chemicals specifically inhibit acidophilic microorganisms (Eklund 1983, Eklund 1980, Cruess and Richert 1929, and Sofos and Busta 1981) and are on the Food and Drug Administration Generally Regarded as Safe (GRAS) List as suitable for inclusion in foods and beverages (U.S. Code of Federal Regulations 1983). On the other hand, small concentrations of SLS may be deleterious to fish and other aquatic life (Margaritis and Creese 1979). Although this potential problem exists with SLS, it has never been detected in any waterway near any of the refuse sites at which the Bureau of Mines has supervised SLS application (Kleinmann and Erickson 1983).

Because various metal sulfides undergo similar chemical reactions (cf. Onysko 1985), inhibition of iron-oxidizing bacteria should also reduce acid production from these wastes. Therefore, the objectives of this study were to determine if these chemicals (surfactants and organic acids) would inhibit the iron-oxidizing bacteria, and if inhibition of these bacteria would reduce acid production.

WASTE MATERIALS

The sulfide tailings used in this experiment came from a metal mine in Quebec, Canada. The ore from this mine is passed through a concentrator and processed for recovery of copper, zinc, pyrite, gold, and silver. The ore passes through multiple stages of crushing, grinding, and flotation. The waste product from the flotation cells constitutes the sulfide tailings (70 pct less than 200 mesh). The extensively weathered tailings used in the experiment were taken from the surface of a large tailings pile. The slightly weathered tailings were taken from under the oxidized layer of the pile.

The waste rock came from a mine in British Columbia, Canada, where the sulfide ore is mined for its silver, copper, and gold content. The material used in the experiment was unprocessed because it was below ore grade. The material was unsized (15 cm x 0 cm) and represented the most acid-producing material from this mine.

Samples of each material were taken at the beginning of the experiment. Total sulfur was measured using the combustion furnace method (American Society for Testing and Materials 1983). To differentiate the sulfur forms, two acid extractions (hydrochloric acid and nitric acid) were performed. The residues from these extractions were analyzed in a combustion furnace, and the percentages of total, pyritic, sulfate, and organic sulfur were calculated (table 1).

EXPERIMENTAL PROCEDURES

The supply of waste materials limited the experiment to three 100-kg samples of each material: one untreated control, one treated with SLS, and one treated with potassium benzoate. In addition to these 100-kg samples, eight 7-kg samples of each material were treated as follows: two untreated controls, a high and low dose of SLS, a high and low dose of potassium benzoate, and a high and low dose of potassium sorbate. The experimental design is summarized in table 2.

For the 100-kg samples, nine 200-L plastic barrels were set up on wooden platforms. Two holes were drilled in the bottom of each barrel, and a plastic bucket was placed underneath each hole to collect leachate. For the 7-kg samples, twenty-four 20-L plastic buckets were used. Each bucket had two holes drilled in the bottom and was

Table 1.--Sulfur content of waste materials.

Material	Sulfur form, pct by weight			
	Total	Pyritic	Sulfate	Organic
Slightly weathered sulfide tailings	20.6	19.7	0.84	-
Extensively weathered sulfide tailings	5.98	0.17	5.81	-
Waste rock	4.07	4.07	-	-

Table 2.--Treatment of samples for each waste material.

Sample weight, kg	Chemical treatment	Treatment dosage, mg/kg	Volume of water used in weekly leachings, L
100	Untreated	-	8.0
100	SLS	600	8.0
100	Benzoate	600	8.0
7	Untreated	-	1.2
7	"	-	1.2
7	SLS	600	1.2
7	"	60	1.2
7	Benzoate	600	1.2
7	"	60	1.2
7	Sorbate	600	1.2
7	"	60	1.2

positioned over another bucket to enable leachate collection.

Each of the mine wastes was used to fill three barrels and eight buckets with 100 kg and 7 kg of material, respectively. The waste materials were added (without compaction) to their respective containers, and within one week, the experiment began. An enclosed hanger-type building in which the air temperature ranged from approximately 15 to 25° C was used for the experiment.

Each barrel (100-kg samples) designated to receive chemical treatment was treated with 8 L of a 7,500-mg/L solution of SLS or benzoate. These treatments were equivalent to 600 mg of treatment chemical per kilogram of waste material, however, any treatment solution that did not adsorb to the waste material was allowed to drain freely from each barrel. The barrels designated as controls received 8 L of deionized tap water.

Two of the eight buckets (7-kg samples) of each material were designated as untreated controls. The remaining six buckets of each material received a high or low dose of SLS, potassium benzoate, or potassium sorbate. The high treatment dose was added to each bucket using 1.2 L of the appropriate 3,500-mg/L solution. The low treatment dose was applied using 1.2 L of a 350-mg/L solution. The high and low treatment doses were equivalent to 600 and 60 mg, respectively, of treatment chemical per kilogram of material. The buckets designated as controls received 1.2 L of deionized tap water.

The weekly leaching program began one week after treatment. Tap water was passed through a 0.20-µm capsule filter and a two-bed ion-exchange-resin system before storage in a 500-gal plastic reservoir. Periodic sampling of this reservoir showed the water to be acceptably low in dissolved solids, and the population of iron-oxidizing bacteria was below detectable limits (<2 cells/100 mL). A plastic sprinkling can was used to distribute water evenly on each waste material. The 100-kg and 7-kg samples were leached with 8.0 and 1.2 L of water, respectively. These volumes are equivalent to 2.5 cm of precipitation on the waste material per week.

After the waste materials were watered, they freely drained into the sample-collection buckets for 24 hours. Samples from each leachate were taken and the remaining volume was measured and discarded. Water samples of the leachate from each bucket and barrel were analyzed for pH, acidity, ferrous iron, total iron, calcium, magnesium, aluminum, sodium, manganese, and sulfate. Ferrous iron was measured by potassium dichromate titration using the sodium salt of diphenylaminesulfonic acid as an indicator. Other metal concentrations were determined by inductively coupled argon plasma (ICAP) spectroscopy. After passing the sample through a cation-exchange resin, sulfate was analyzed by barium chloride titration using thorin as an indicator. Acidity analysis consisted of a fixed endpoint titration to pH 8.3 using a 1N sodium hydroxide solution and converted to mg/L as $CaCO_3$.

Analyses for iron-oxidizing bacteria were performed for the 100-kg samples (barrels) only. The multiple-tube, most probable number (MPN) method (American Public Health Association 1985) using the media described by Cobley and Haddock (1975) was used. This method uses a series of 10-fold sample dilutions that are added to a low-pH, ferrous-iron-enriched media. Bacterial densities are estimated by observing a color change in the tubes, which indicates oxidation of ferrous iron by iron-oxidizing bacteria.

The percent of iron in the ferrous (as opposed to ferric) state in the raw samples was found to be a good indicator for the density of iron-oxidizing bacteria. Higher ferrous iron percentages indicated that the bacterial density was low. Conversely, lower ferrous iron percentages indicated higher numbers of bacteria. Therefore, chemical analysis of the leachate (for ferrous and total iron) enabled a rough estimate of the number of iron-oxidizing bacteria in the 7-kg samples without actual MPN analysis. Figure 1 shows these correlations for the 100-kg samples of waste rock and slightly weathered sulfide tailings that were treated with SLS.

RESULTS

The following sections cover the results of the three treatment chemicals on the three mine waste materials. Although direct measurements of the bacterial populations were made, the effectiveness of the chemicals was based on leachate water quality. Graphs of acidity concentration and cumulative acid load over time are presented because acidity directly relates to water treatment costs and acidity was correlated with other water quality parameters of interest (table 3). All acidity measurements are expressed in $CaCO_3$ equivalence.

Table 3.--Spearman's correlation coefficients* of acidity with other water quality parameters.

Sulfate	0.97
Iron	0.94
Aluminum	0.94
Manganese	0.89
pH	-0.78

*All significant at $p < 0.001$

Waste Rock

In the 100-kg samples, the iron-oxidizing bacteria were reduced below detectable limits by SLS and benzoate for 182 and 231 days, respectively (fig. 2). Both SLS and benzoate significantly reduced acidity levels in the leachate (fig. 3). After 250 days, the cumulative acid load generated by each treated sample was 15 percent of the cumulative acid load generated by the control (fig. 4). Forty days after the bacterial inhibitors began to lose effectiveness, the iron-oxidizing bacteria repopulated to levels greater than those found in the control. The concentration of acidity from each treated sample also increased above the control level. These increases in acidity occurred about 100 days after the increases in iron-oxidizing bacteria.

In the 7-kg samples, the high dose (600 mg/kg) of SLS, benzoate and sorbate kept acidity concentrations below 50 pct of the lowest of the two untreated controls for 343, 147, and 147 days respectively (fig. 5a). The low dose (60 mg/kg) of SLS and benzoate reduced acidity concentrations below 50 pct of the lowest control for 63 and 77 days, respectively. The low sorbate dose did not reduce acidity levels (fig. 5b).

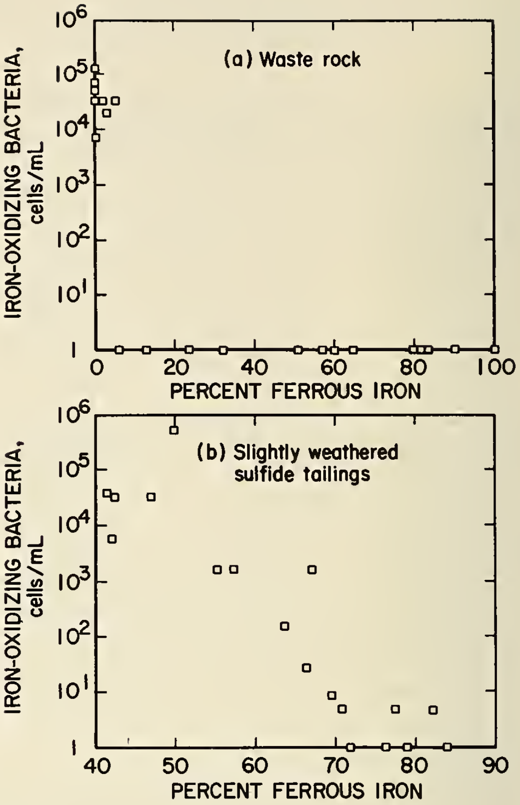

Figure 1.--Relationship between the population of iron-oxidizing bacteria and percent ferrous iron in 100-kg, SLS-treated samples of (a) waste rock and (b) slightly weathered sulfide tailings.

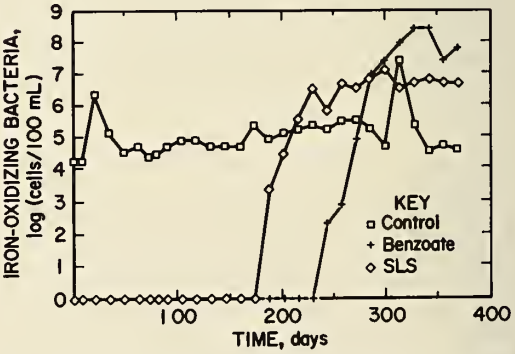

Figure 2.--Population of iron-oxidizing bacteria vs. time for 100-kg samples of waste rock.

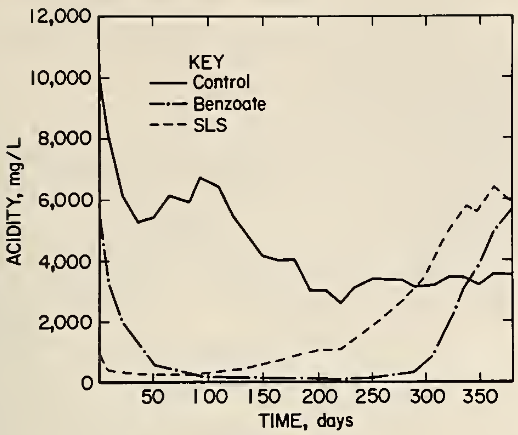

Figure 3.--Acidity concentration vs. time for 100-kg samples of waste rock.

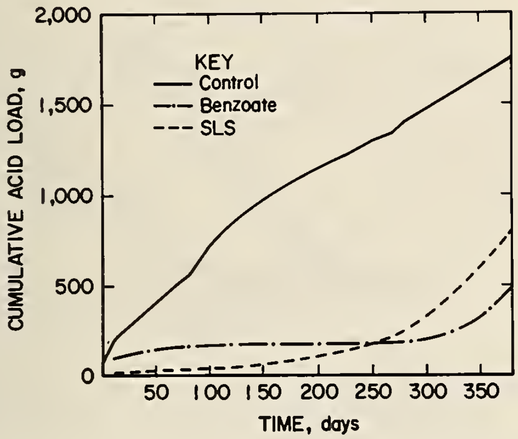

Figure 4.--Cumulative acid load vs. time for 100-kg samples of waste rock.

Extensively Weathered Sulfide Tailings

In the 100-kg samples, greater concentrations of acidity were leached from the SLS- and benzoate-treated samples than from the control in the first 40 to 56 days (fig. 6). Bacterial populations were not inhibited, and ranged from 3 x 10^3 to 2 x 10^5 cells/100 mL.

Similarly, results from the 7-kg samples showed that all of the treatments increased acidity over control levels in the first 28 to 56 days of the experiment with no subsequent difference in acidity levels between treated samples and controls for the remainder of the experiment. Ferrous iron data suggested that no significant bacteria inhibition occurred.

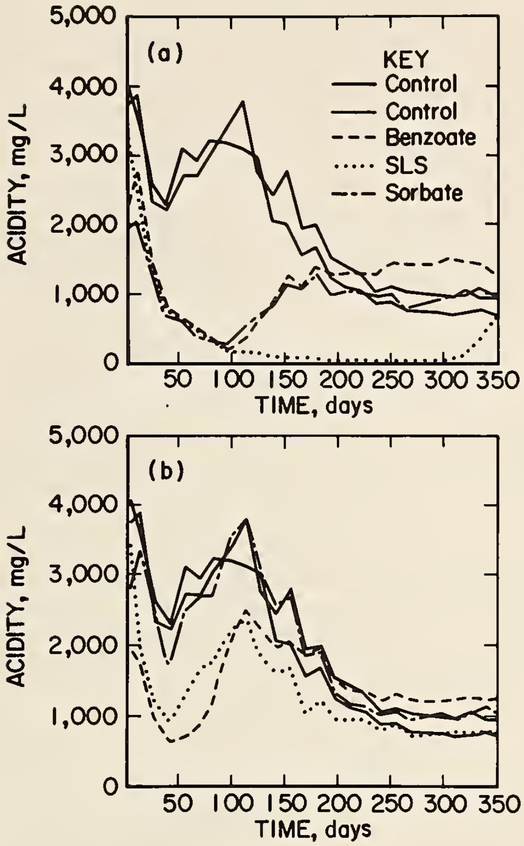

Figure 5.--Acidity concentration vs. time for (a) high treatment dose (600 mg/L) and (b) low treatment dose (60 mg/kg) on 7-kg samples of waste rock.

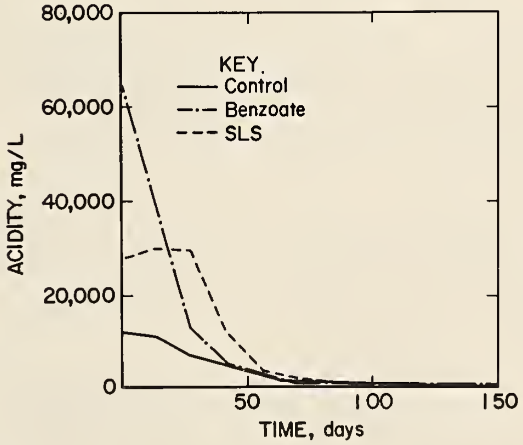

Figure 6.--Acidity concentration vs. time for 100-kg samples of extensively weathered sulfide tailings.

Slightly Weathered Sulfide Tailings

In the 100-kg samples, neither SLS nor potassium benzoate reduced acidity levels relative to the control in the leachate from the slightly weathered sulfide tailings. However, both treatments kept the bacterial population significantly below that of the control for approximately 130 days (fig. 7). In the 7-kg samples, none of the treatments had any significant effect on leachate water quality. However, based on the high percentages of total iron remaining in the ferrous form, the iron-oxidizing bacteria were inhibited for over 100 days.

An additional test was performed to determine why the inhibition of bacteria in the slightly weathered sulfide tailings did not result in lower acidity levels. In this test, the tailings were washed with a dilute hydrochloric acid solution to remove any oxidized products before the treatments were added. The experiment used six 7-kg samples, three of which were not treated with bacterial inhibitor to act as controls. Two samples were treated once with a 600 mg/kg dose of SLS and one sample was treated once with a 600 mg/kg dose of benzoate. Procedures used for leaching and water quality analyses were the same as outlined in the experimental procedure section.

Both SLS and benzoate significantly reduced acidity below control levels (fig. 8). At the end of 150 days, the cumulative acid load generated by each treated sample was 18 percent of the acid loads produced by the control samples (fig. 9). Analysis for iron-oxidizing bacteria showed that populations in the SLS- and benzoate-treated samples remained below 2 cells/100 mL for 112 and 98 days, respectively. The population of iron-oxidizing bacteria in the control samples ranged from 2.3 x 10^4 to 1.3 x 10^5 cells/100 mL.

DISCUSSION

The leaching procedure used in this experiment represents an acceleration of actual field rainfall conditions. Although 2.5 cm/week of precipitation does not seem excessive, the procedure does not allow for runoff or evaporation that might occur in the field. The duration of bacterial inhibition for the treatment chemicals may have been diminished by the short period of time that the water was added. This may have increased the amount of chemical that was washed off; however, the treatment was not lost to runoff and may have been deposited at a lower position in the sample. Because of these variables, caution must be exercised during extrapolation of the results of laboratory leaching tests to intended field use.

Results from the benzoate- and SLS-treatments of the waste rock indicate that both chemicals may be applicable for field use. SLS has reportedly been applied to waste rock by a mining company in the field, but no reductions in contaminant levels were observed. The blocky nature of the waste rock permits air to penetrate deeply into the pile. Consequently, in order to inhibit bacteria and reduce contaminant levels, a large portion of the pile must receive the chemical inhibitor and not just the uppermost layer.

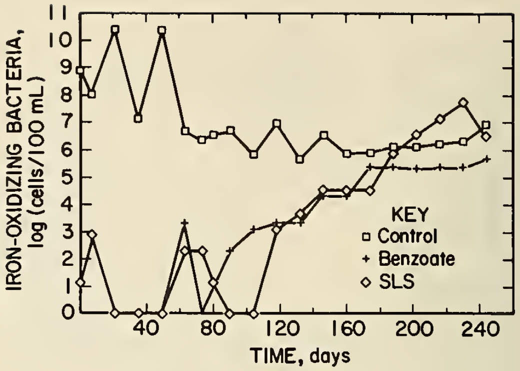

Figure 7.--Population of iron-oxidizing bacteria vs. time for 100-kg samples of slightly weathered sulfide tailings.

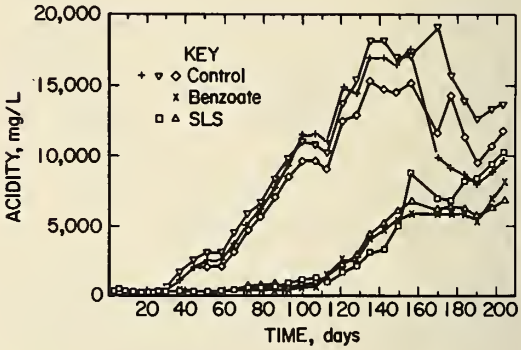

Figure 8.--Acidity concentration vs. time for 7-kg samples of hydrochloric-acid-rinsed sulfide tailings.

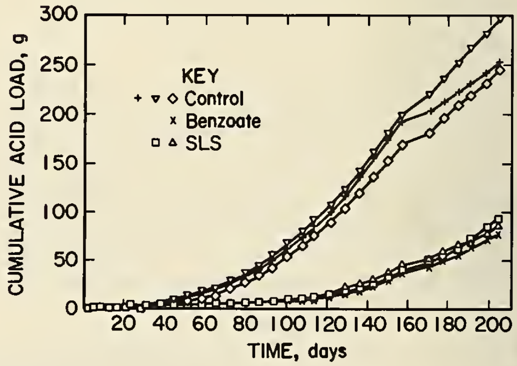

Figure 9.--Cumulative acid load vs. time for 7-kg samples of hydrochloric-acid-rinsed sulfide tailings.

Results from the extensively weathered sulfide tailings showed that all of the treatments increased acidity levels in 100- and 7-kg samples. The material was considerably oxidized with 5.81 pct sulfate sulfur and only 0.17 pct pyritic sulfur; therefore, most of the contamination in the leachate was from the flushing of previously oxidized material. Apparently, the treatment chemicals caused an increased flushing of contaminants. SLS could have increased contaminant flushing by its surfactant properties. Benzoate and sorbate readily form complexes with iron which could result in dissolution of weathered products, thereby increasing contaminant flushing.

The results from the slightly weathered sulfide tailings showed that SLS, benzoate, and sorbate effectively inhibited iron-oxidizing bacteria but did not reduce contaminant levels. However, in a subsequent test in which the tailings were washed with dilute HCl to remove any oxidized products prior to treatment, SLS and benzoate inhibited the bacteria and reduced acidity levels. These results indicate that these chemicals may be applicable to field use if the tailings can be treated before they begin to oxidize.

In all three materials, differences between the results from the 100-kg samples and the 7-kg samples were noted. In the 100-kg samples of extensively weathered sulfide tailings, SLS and benzoate initially increased acidity to 28,000 and 67,000 mg/L, but the leachate from the control sample only contained 12,000 mg/L; however, in the 7-kg samples initial acidity levels were only 18,000 mg/L for the treatments compared to 10,000 and 15,000 mg/L for the two controls. Likewise, in the 100-kg samples of the slightly weathered sulfide tailings, much larger increases in acidity levels for the treated samples were observed in the larger scale test than in the 7-kg samples. Also, the magnitudes of acidity concentration were much larger from the 100-kg samples (up to 150,000 mg/L) than from the 7-kg samples (below 25,000 mg/L). In the waste rock, using the 600 mg/kg dose of treatments, the 100-kg samples showed benzoate to be slightly more effective than SLS, but in the 7-kg samples, SLS was much more effective than benzoate. Again, magnitudes of contaminant concentration differed between the two sample sizes. Although basic trends were fairly consistent between the 7- and 100-kg sample results, large discrepancies in contaminant concentration were observed even under these controlled conditions. Therefore, trying to use this laboratory data to extrapolate to anticipate field results (viz. correct chemical treatment dose, duration of effectiveness, reduction of acidity and metals levels, and corresponding reduction in water treatment costs) cannot be accurately made. However, these methods can be used to screen potentially effective chemicals and provide some guidance for larger scale field studies.

CONCLUSIONS

The amount of weathering a mine waste has undergone prior to treatment with SLS, potassium benzoate, or potassium sorbate determines the effectiveness of these chemicals to inhibit iron-oxidizing bacteria. Application of these chemicals on weathered mine wastes can increase the liberation of previously oxidized contaminants. The presence of even a small amount of weathered products on mine wastes can render these treatments ineffective. However, if the material is unweathered (all sulfur in the pyritic form), these treatments can inhibit iron-oxidizing bacteria and significantly reduce acidity, sulfate, and metal concentrations in the leachate.

In our tests using sulfide tailings, SLS, potassium benzoate, and potassium sorbate did not reduce contaminant concentrations in the leachate from the any of the weathered tailings. However, following removal of the weathered products from the slightly weathered sulfide tailings, SLS and benzoate effectively reduced contaminant concentrations in the leachate. Respectively, SLS and benzoate reduced the density of iron-oxidizing bacteria below detectable limits (2 cells/mL) for 100 and 86 days, and reduced the cumulative acid load to 18 percent of the control acid load after 150 days.

Results of the tests using 100-kg samples of waste rock showed that SLS and potassium benzoate inhibited the iron-oxidizing bacteria below 2 cells/100 mL for 182 and 231 days, respectively. In these samples, SLS and benzoate reduced the cumulative acid load to 15 percent of the acid load from the control after 250 days.

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MAPPING BURIED TIPPLE REFUSE - IS THE MAGNETOMETER BETTER THAN TERRAIN CONDUCTIVITY?[1]

Joseph H. Schueck, P.E.[2]

Abstract.--It is occasionally desirable to detect and map tipple refuse buried beneath strip mines. Reasons include: acid mine drainage (AMD) treatment and/or abatement, and economic recovery for reprocessing. Until now terrain conductivity (EM) has been the most efficient, cost effective method of mapping refuse. However, it is difficult to delineate between refuse and other features such as AMD using EM. Remanent magnetism, a property somewhat 'unique' to refuse in the strip mine environment allows refuse to be mapped independently of other features using a magnetometer. Two sites were mapped using both EM and the magnetometer. Refuse disposal completely filled large pits at the first site but was limited to widely scattered, small pods at the second. When the proper grid density was used, the EM was able to define general disposal areas but was unable to pinpoint refuse locations, especially on the site where the refuse was in scattered pods. The EM was unable to discriminate between the refuse and AMD. On the other hand, the magnetometer was able to clearly define the refuse limits on both sites without interference from the AMD. Acquisition of data is seven times faster with the magnetometer and the magnetometer data provides much better quantitative information about the refuse than does the EM data.

INTRODUCTION

Many advances have been made in recent years toward preventing, mitigating, abating, and treating acid mine drainage. Research efforts have concentrated on the source of the acid mine drainage as well as the discharge. Buried tipple refuse is a source of many acid mine drainage discharges. However, treatment at or elimination of the source cannot be accomplished until the refuse has been delineated. Additionally, refuse from certain older plants may be rich enough to be reprocessed, provided it can be found and mapped efficiently. This paper discusses a rapid and efficient method to accurately map buried tipple refuse.

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Tipple refuse is commonly disposed of at both active and abandoned strip mines. Pits may be completely filled with refuse at abandoned sites, and the refuse 'pods' or buried piles may be quite large. At active sites burial locations are dictated by the location of the working pit. Widely scattered pods of limited aerial extent commonly result. Following reclamation, there is little evidence to indicate the locations of the buried refuse. Producing accurate maps of these locations has been difficult until now.

Subsurface features on strip mines have been successfully mapped in recent years using geophysical techniques such as DC electrical resistivity and electromagnetic terrain conductivity (EM). Refuse usually responds well to both methods if it is an electrical conductor. However, features such as subsurface accumulations of acid mine drainage also conduct electricity well and may produce anomalies similar to refuse. This property makes delineation of refuse difficult using either method.

Another property of at least some refuse, magnetism, allows the refuse to be detected with a magnetometer. Magnetometer operation requires only one person. It will be shown that buried refuse can be mapped in greater detail and several times faster with a magnetometer than with EM or DC resistivity.

Two sites, referred to as SW1 and NW1, were mapped during this study. Tipple refuse was buried in abandoned strip mine pits at SW1. The resultant pods of refuse were up to 700 ft long. Refuse was buried in scattered pods controlled by the location of active pits on NW1. The majority of these pods probably are no larger than one or two truckloads of refuse. Magnetic detection of the buried refuse at both sites was quite successful.

PRINCIPLES OF MAGNETISM

The earth's magnetic field resembles the field of a large bar magnet near its center. Flux lines of the earth's field exhibit a pattern like that of a bar magnet, figure 1. The field intensity is a function of the flux line density. Similar to a bar magnet, the density is twice as large in the polar regions as in the equatorial regions, or approximately 60,000 and 30,000 gammas respectively. The total field is approximately 55,500 gammas in Pennsylvania. By convention in the geophysical community, gauss is the cgs unit of magnetic intensity and 1 gamma=10^{-5} gauss. The earth's total magnetic field intensity is measured using a magnetometer (Breiner 1973). Most commercially-available magnetometers measure the magnitude of the total field intensity. Older, "fluxgate"-type, magnetometers are sometimes seen. These measure components of the total field intensity vector.

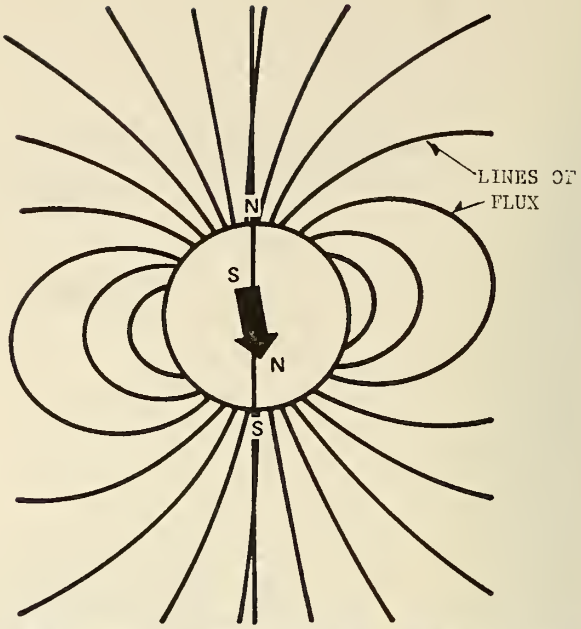


Figure 1. The earth's magnetic field resembles the field of a large bar magnet. The flux line density is greater at the polar regions than at the equator (Breiner 1973).

An anomaly represents a local disturbance in the earth's magnetic field due to a local change in magnetization. Magnetic minerals and iron have properties which cause these anomalies. Natural anomalies are due chiefly to the presence of magnetite ($FeFe_2O_4$), or its related mineral suite: ulvospinel, maghemite, etc. All rocks contain some magnetite from a very small fraction of a percent up to several percent. Iron objects produce strong, local magnetic anomalies (Breiner 1973).

Magnetic anomalies are caused by two different kinds of magnetism: induced and remanent or "permanent" magnetization. Induced magnetization refers to the effect on a material placed in an external magnetic field in which the field within the material is enhanced, so that the material itself acts as a magnet. Induced magnetization is always parallel to the inducing field (usually the earth's), and would vanish if this inducing field were removed. The magnetization of such material is directly proportional to the intensity of the ambient field and to the ability of the material to enhance the local field. This property is called magnetic susceptibility. The induced magnetization is equal to $I_i=kF$, where I_i is the induced magnetization per unit volume in cgs electromagnetic units, k is the volume magnetic susceptibility, and F is the field intensity in gauss. k is usually between 10^{-6} and 10^{-3} cgs or for most rocks. For pure magnetite, k is approximately 0.3 cgs. k may vary between 1 and 10^{6} for iron alloys(Breiner 1973).

Materials cooling from high temperatures may attain a remanent magnetization. This remanent magnetization, once gained, is independent of external fields..it need not be parallel to the external field and will remain even if the external field is removed. Remanent magnetization, I_r, is often ten or more times greater than induced magnetization in many igneous rocks and iron alloys. Permanent magnetization depends upon the metallurgical properties and the mechanical, thermal, and magnetic history of the specimen. Prior to heating, small regions, called domains, within each magnetite crystal are randomly oriented. The domains reorient themselves during heating. Upon cooling, they align parallel to each other in the direction of the ambient magnetic field. This creates a net magnetization fixed with respect to orientation of the object. Magnetite may have a remanent magnetization, I_r, of perhaps 0.1 to 1.0 gauss (10^4 to 10^5 gammas). Ordinary iron may have a permanent magnetization between 1 and 10 gauss (10^5 and 10^6 gammas). Thus the net magnetization might be considerably higher and oriented in a different direction than would be indicated merely by consideration of the susceptibilities (Breiner 1973).

SOURCES OF MAGNETISM IN TIPPLE REFUSE

Samples of refuse and spoil material from both sites were analyzed to determine the magnetic components unique to the refuse. The samples were obtained by air rotary drilling. A magnetic separator, known as a ferrofilter, was used to remove the magnetic portion of the sample. In all cases the magnetic portion of the sample amounted to only a small fraction of a percent. Two magnetic materials were identified: magnetite crystals ($FeFe_2O_4$), and reddish grains and black glassy B.B.'s that appear to be combustion products containing magnetite or maghemite (Fe_2O_3) unintentionally synthesized during combustion (Smith 1987). These particles commonly exhibited a 'slag'-like appearance and were often fused with quartz crystals. The portions of the samples which had undergone combustion were so minute that they were not detected in an unfiltered sample using a hand lens. Maghemite forms by slow oxidation at low temperatures from magnetite or from the slow thermal dehydration of lepidocrocite (FeO(OH)) below temperatures of 750°. The magnetic properties of maghemite are similar to those of magnetite (Palache, et. al 1944). Company officials from both source tipples indicated that the source plants used magnetite in the coal separation process at the time the refuse was buried on the subject sites.

An increase in the net magnetism caused by the combustion or heating and dehydration of the refuse appears to be a significant factor in the magnetometer's ability to detect refuse. Microscopic examination of several samples indicates that magnetite is common at SW1 where refuse was buried in large pods. Combustion products are also present but are uncommon. By contrast, at NW1, combustion products are common and magnetite crystals are rare. The recorded intensities per unit mass of refuse were much higher at NW1 where the combustion products are predominant than they were at SW1 where magnetite is predominant.

MAGNETIC ANOMALY CHARACTERISTICS

Magnetic anomalies are highly variable in shape and amplitude; they are almost always asymmetrical, sometimes appear complex even from simple sources, and usually portray the combined magnetic effects of several sources. An anomaly's shape or signature depends upon the inclination of the field, and several properties of the source: burial depth, size and shape of the source, the relative amounts of permanent and induced magnetization, the direction of the former, and the amount of magnetic material present in the source compared to the adjacent rocks (Breiner 1973).

The dip or inclination of the earth's field establishes the direction in which the components are measured for any local magnetic anomalies using a total field magnetometer. The magnetometer only measures the component of a local disturbance in the direction of the earth's field at the point of measurement, figure 2. Other factors being equal, the same source will produce three different anomaly signatures if measured at the equator, in Pennsylvania, and near the north pole.

The variation of intensity as measured by the magnetometer diminishes as the source-to-sensor distance increases. Depending on the shape of the source body, this fall-off factor usually goes as $1/r^3$ to $1/r^2$, where r is the distance between the source and the sensor. For this reason, anomalies will be larger in aerial extent than the actual source of the anomaly, figure 3.

The depth to and configuration of the source determines the anomaly wavelength; the deeper and larger the source, the broader the anomaly. Sources close to the ground surface exhibit a steep gradient between the negative and positive portions of the anomaly. Deeper sources exhibit a much flatter gradient. Figure 4 shows two anomalies which were mapped. The depth to the source on the left is about 12.5 ft compared to a 50 ft burial depth on the right.

The negative part of an anomaly is called its "polarity low". At the latitude of Pennsylvania, a body whose

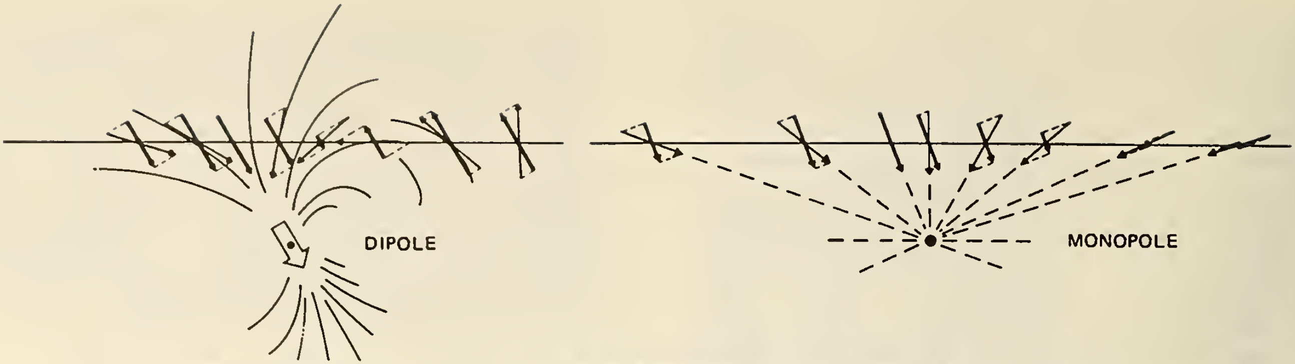


Figure 2. The portable proton magnetometer only measures the component of a local disturbance in the direction of the earth's field at the point of measurement (Breiner 1973).

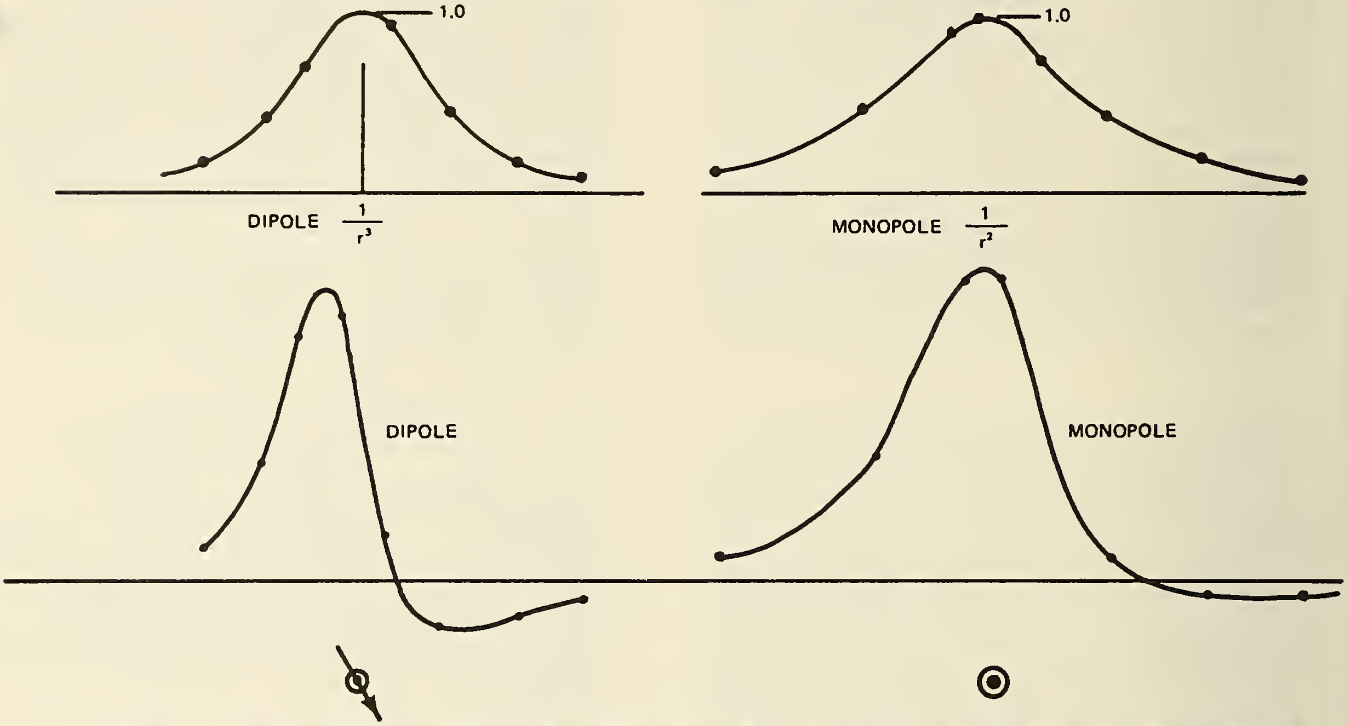


Figure 3. The variation of intensity as measured by the magnetometer diminishes as the source-to-sensor distance increases. The fall-off factor usually goes as $1/r^3$ for dipoles to $1/r^2$ for monopoles. Resultant anomaly signatures are shown at the bottom of the figure for dipoles, left, and monopoles, right (Breiner 1973).

magnetization is mostly induced will usually have a small polarity low to the magnetic north, with the maximum part of its high over the southern part of the body. A body with very strong remanent magnetization, by contrast, will have an adjacent polarity low in some direction other than north. If such a pattern is seen on a magnetic map, it usually indicates sources with strong remanence.

Maximum anomaly amplitude depends upon several factors. These include depth, the contrast in the mass of magnetic material to the surrounding material, and the shape and configuration of the source. Small, compact sources will appear as a dipole, i.e. the anomaly signature will show both an anomaly high and a polarity low. If the source is narrow, broad, or long in one dimension, the anomaly may appear as a monopole, i.e. only a positive portion may be recorded or the polarity low may appear beyond one of the ends.

FIELD PROCEDURES

A portable proton magnetometer was used at both sites. This instrument measures total field intensity only. It has a sensitivity of + or - 1 gamma over a range from 20,000 to 90,000 gammas and a gradient tolerance which exceeds 800 gammas/ft. The instrument consists of a sensor mounted on a 8-ft long staff connected to a power pack and digital readout display (Geometrics).

A grid network along with a base station or baseline should be established over the site before readings are taken. Grid spacing depends on the anticipated

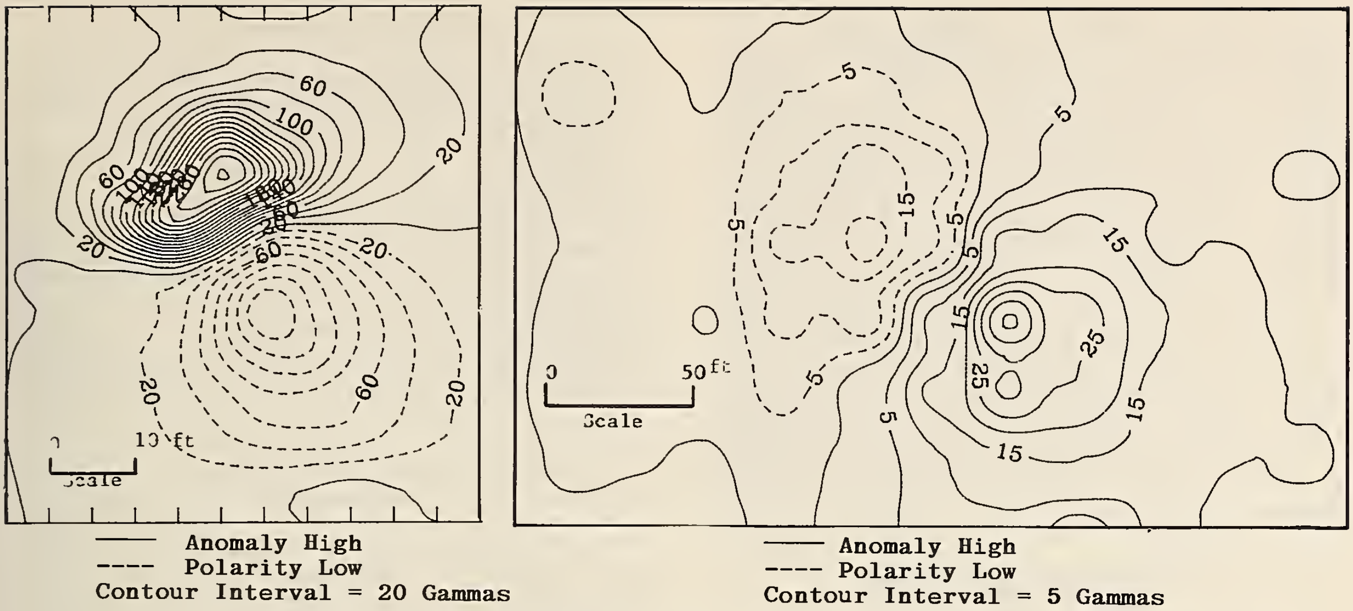


Figure 4. The depth to and configuration of the source body controls the anomaly signature. The deeper and larger the source body, the broader the anomaly. Shallow sources exhibit a steep gradient between the anomaly high and the polarity low; deep sources produce a flat gradient. The depth to the source body on the left is 12.5 ft compared to a 50 ft burial depth on the right. Note scale and contour interval differences.

target size. Readings are taken along the grid intersections with frequent measurements made at the base station or along the base line.

Magnetometer operation is quite simple. The staff with the sensor mounted on top is placed on the ground at the point where the reading is to be taken and is held still. A read button is pushed. Seconds later a digital readout appears which is recorded. The sequence is repeated at each grid intersection. Data acquisition is quite rapid. However, a few precautions must be taken in order to insure meaningful data.

Quality control is a key to obtaining reliable field data. A proper grid density must be selected, natural variations in the earth's field intensity must be tracked, and local magnetic anomalies not associated with the target must be located and noted.

The aerial extent of the refuse dictates the maximum grid spacing or station density which may be used. Large pods on the order of tens or hundreds of feet can be adequately mapped on a 25 by 50 ft grid. Truck load sized pods of refuse can be located with a 25 by 25 ft grid; however, reasonable definition of the refuse requires returning to the target area and taking additional readings on a tighter grid.

Recording variations in the earth's total field with time and removing these variations from the field data are crucial to quality data. Magnetic storms and micropulsations due to solar winds acting on the ionosphere cause variations of 10's to 100's of gammas. These variations are not predictable. They may occur over a short period of 10's of minutes and be quite irregular or they may occur slowly over a period of a day (Breiner 1973). A recording base station magnetometer on or near the site can record these variations while field readings are being taken elsewhere. The base station readings are then used to correct the field readings. Otherwise it is necessary to establish a base station or base line and return to the station frequently, usually after every traverse, to record the variations. Figure 5 shows a variation of nearly 35 gammas which occurred at the base station on SW1 over an 8-hour time span. Daily variations such as this were common at both sites.

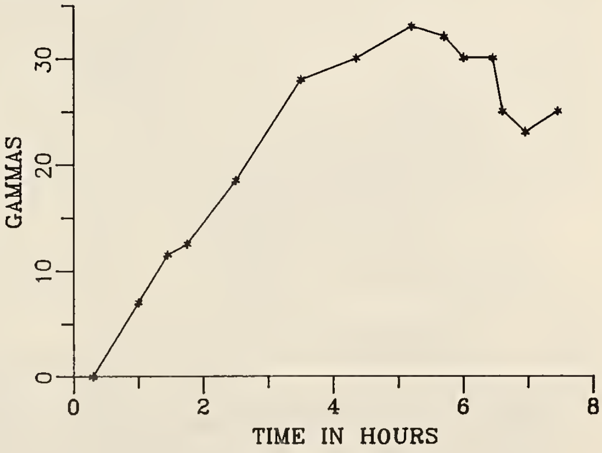


Figure 5. Normal Daily Magnetic Fluctuations

Scrap metal and other iron objects lying on the surface must be removed to an area beyond their influence on the readings. Locations of metal objects which cannot be removed from the area, such as well casings, should be noted and their influence taken into consideration during the interpretation. Examples of such interferences follow. At NW1 small plastic flags on wires were used to mark grid locations. Readings obtained adjacent to these flags resulted in 10 to 15 gamma anomalies. A metal well casing and a galvanized garbage can produced 225 and 170 gamma anomalies, respectively, with the magnetometer adjacent to the metal. The anomalous reading diminished to 0 at about 20 ft in both cases. A drag line cable buried just beneath the surface caused a 10,000 gamma anomaly on another site.

FIELD STUDY AT SW1 SITE

Site Description

SW1 is a 43 acre reclaimed refuse disposal site in Somerset County, Pa. Once an active strip mine, the original operator abandoned the site after coal removal, leaving behind several unreclaimed pits and spoil piles. The pits were as deep as 60 ft and several were longer than 500 ft. Pit width varied from 50 to 200 ft. Some pits had vertical unreclaimed highwalls while others had sideslopes of spoil.

All major pits on the site were later permitted for tipple refuse disposal. Inspection reports and subsequent drill holes indicate that the operator completely filled the pits with refuse. The site was then regraded and reclaimed by this operator, leaving no surficial evidence of the buried refuse locations.

Conductivity Field Work

The southern half of SW1 was mapped in 1986 using electromagnetic terrain conductivity. The purpose was to determine the refuse limits so that monitoring wells could be strategically located. The area was mapped on a 50 by 50 ft grid and a total of 191 readings were made. A 10-m intercoil spacing with a horizontal coplanar dipole configuration was used. It was known that burial of the refuse extended to near the surface. This configuration has an effective exploration depth of 7.5 m and is more responsive to the near surface material (McNeill 1980).

Conductivity Survey Results and Interpretation

A contour map of the EM data is shown in figure 6. Delineation of the refuse from the EM data was difficult for two reasons. First, the conductivity values ranged from a low of 5.5 to a high of 17.5 mmhos/m. Conductivity measurements over refuse are commonly in the 20 to 40 mmhos/m range on many sites, especially considering the thickness and extent of the refuse here(Ladwig 1982). Second, a rapid increase in the conductivity contour gradient was not observed, making boundary determinations difficult. This suggests a gradual thickening of the refuse, as is the case. The contours did steepen slightly beyond 8.5 mmhos/m, and it was decided that values greater than this probably indicated refuse.

Highs on the EM contour map correspond fairly well with outlines of the pits scaled from aerial photos taken prior to refuse disposal. These boundaries compare well with the pit limits indicated on the permit maps. The maximum conductivity values generally coincide with or lie just to the north of

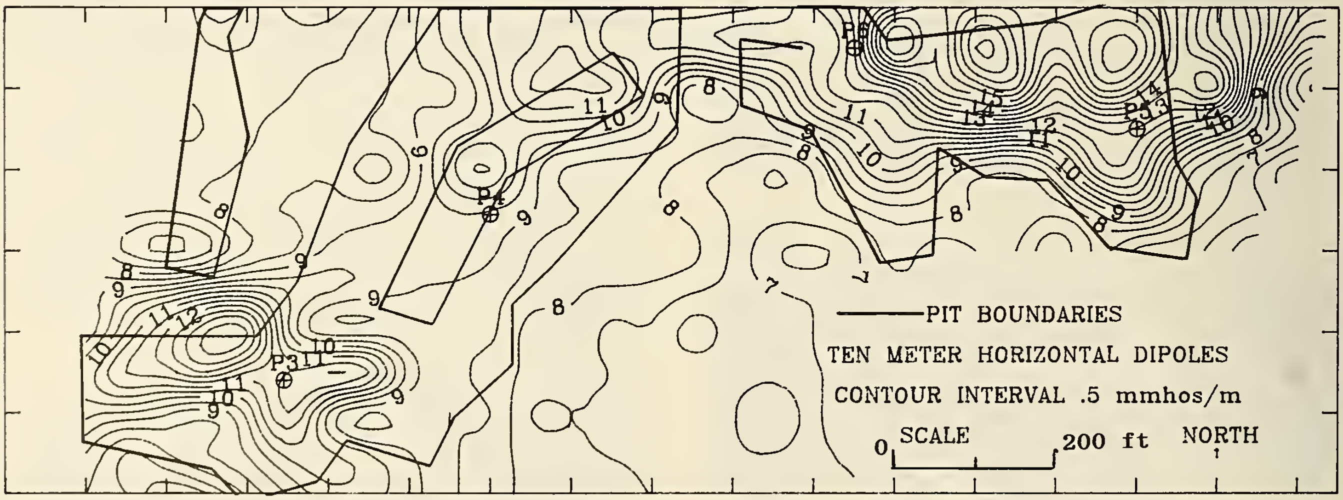


Figure 6. Electromagnetic Terrain Conductivity contour map resulting from the survey conducted on the southern half of the SW1 coal refuse disposal site. A 10-m horizontal dipole coplanar configuration was used. Refuse was disposed of within the pit boundaries which are indicated. Note the absence of rapid contour steepening and conductivity highs beyond the pit boundaries.

the deepest portions of the pits. Four monitoring wells were subsequently drilled within areas interpreted to be refuse. Refuse depths and thicknesses as indicated in the four wells correlate well with the conductivity data.

There are high conductivity values in two areas where very little refuse, if any, is thought to exist. The first is to the north of the pit in the southwestern corner. This area is on the nose of a steep pre-disposal spoil pile. The amount of refuse in this location should be minimal. The second area is to the east of the pit in the northeastern portion of the study area. Aerial photos indicate pre-disposal spoil piles in this area also. It is unlikely the operator excavated into the spoil to dispose of refuse. These values may indicate areas of AMD, however.

A maximum conductivity value of 12 mmhos/m is observed in the vicinity of well P4. This long narrow pit is filled with refuse to a total depth of 60 ft. By comparison, the maximum value observed over the pit to the east containing wells P6 and P5 is 17.5 mmhos/m. The thickness of the refuse in this pit is also 60 ft. The low value of 12 mmhos/m is misleading, but this may be a function of the pit geometry.

Magnetometer Field Work

SW1 was remapped in June 1987 using a portable proton magnetometer borrowed from the Pa. Geologic and Topographic Survey. The limits of the study were extended northward to cover the entire 43 acres. Readings were initially taken on a 50 by 25 ft grid. Some areas were remapped on a 25 by 25 ft grid for better resolution.

Magnetometer Survey Results and Interpretation

The magnetic anomaly map for SW1 is presented in figure 7. The positive anomalies are shown as solid lines. Dashed lines indicate the polarity lows. The pit boundaries are also indicated as in figure 6. Two basic anomaly signatures are repeated: 1) relatively flat gradient, maximum 40 gamma anomalies over the long pits to the northwest, and 2)relatively strong positive anomalies with steep gradients and maximum values of about 200 gammas over the pits in the southwestern and eastern portions of the figure. Keep in mind that the refuse pods in this figure are somewhat smaller than the area of the anomalies they cause. Considering this, the positive magnetic anomalies correlate quite well with the pit locations despite the different anomaly signatures that are present.

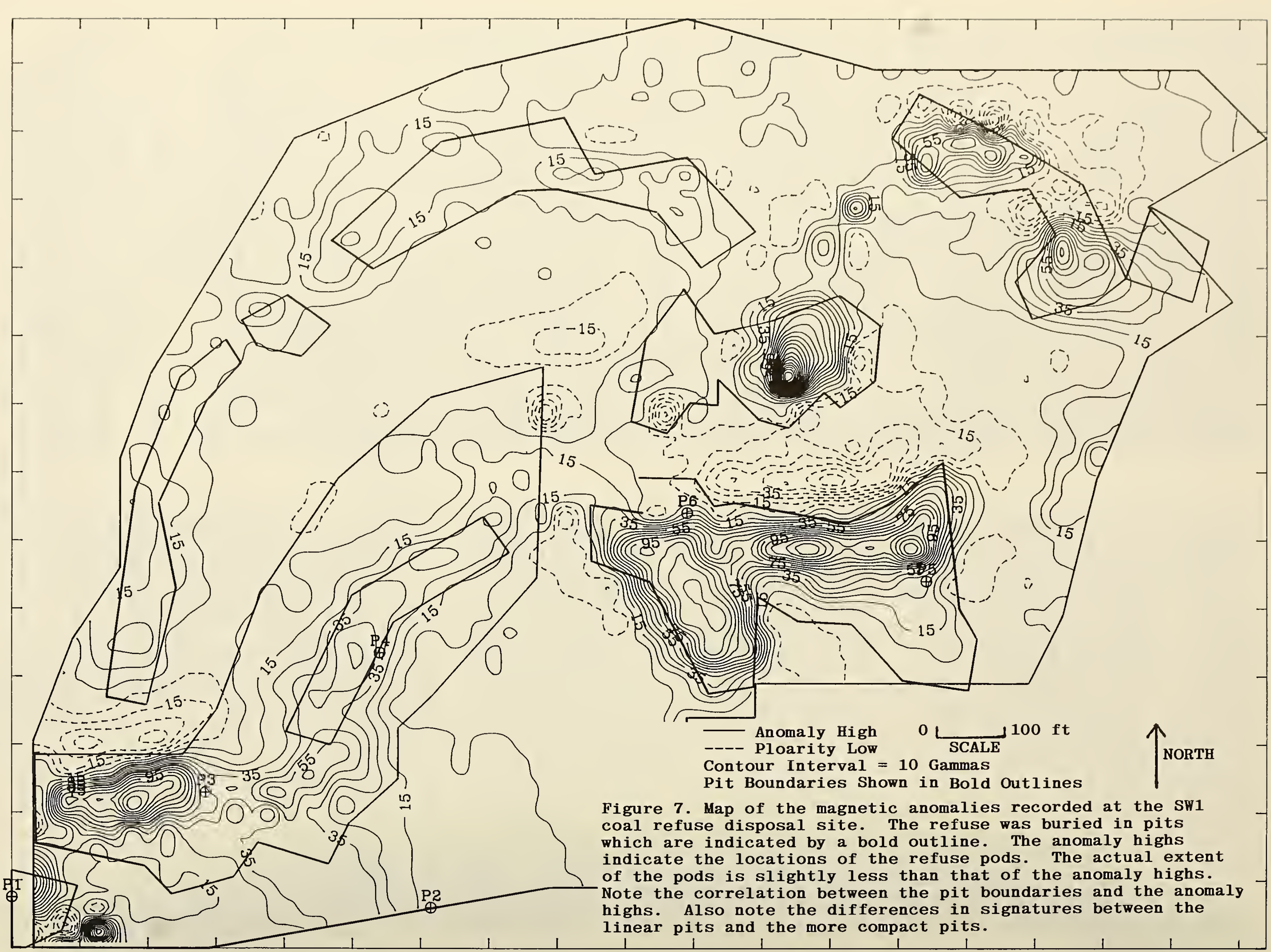
The anomalies over the northwestern pits are consistent with the signatures expected over long, narrow dike-like structures. The anomaly signature is like that of a line of monopoles, i.e. there is no distinct polarity low associated with the anomaly. Because the magnetometer measures the net magnetization of the mass within the radius of influence, the maximum amplitudes over long, narrow structures will be less than that observed over wider structures of similar total depth.

The anomaly signatures over the remaining pits are also consistent with those expected for wide, thick source bodies buried at a shallow depth. The prominent polarity lows to the north of these highs suggest their net magnetization is aligned with the earth's field, and so may be dominantly of the induced kind. The magnetic components of the source bodies here are therefore inferred to consist largely of magnetite rather than combustion products. It is further inferred that the magnetite's domains of permanent magnetization were randomized when the refuse was dumped in the pits. The high amplitude of the anomaly implies a relatively higher concentration of magnetic materials in these pits than in those to the northwest.

The southeastern pit in figure 7 is presented in figure 8 to illustrate how the observed values correspond to thickness of the source body. Lines indicating the pit boundary, pit bottom, and spoil pile intersections are included. Coal pavement was exposed in the western portion of the pit prior to filling with refuse. A vertical highwall of bedrock formed the western pit boundary. The eastern portion of the pit was formed by spoil piles at their angle of repose joining near the center of the pit. The haul road into the pit was located in the extreme northwestern corner of the pit where no boundary line is shown. Refuse completely fills this pit to within a few feet of the surface. The refuse over the pavement in the western portion of the pit extends from near surface to a depth of 60 ft. The depth of refuse in the east-west trending portion of the pit with sloping sides formed from spoil approaches a maximum of 60 ft while the depth of refuse in the southeastern portion is less than 40 ft. The magnetic map, therefore, appears to reflect many of the geometric details of the original pit.

Comparison of EM and Magnetometer Results

Clearly the magnetometer has defined the refuse more accurately than the EM, both qualitatively and quantitatively. The two areas beyond the pits in figure 6 which could easily be



—— Anomaly High
---- Ploarity Low
Contour Interval = 10 Gammas
Pit Boundaries Shown in Bold Outlines
0
100 ft
SCALE
NORTH
P1
P2
P3
P4
P5
P6
15
35
55
95

Figure 7. Map of the magnetic anomalies recorded at the SW1 coal refuse disposal site. The refuse was buried in pits which are indicated by a bold outline. The anomaly highs indicate the locations of the refuse pods. The actual extent of the pods is slightly less than that of the anomaly highs. Note the correlation between the pit boundaries and the anomaly highs. Also note the differences in signatures between the linear pits and the more compact pits.

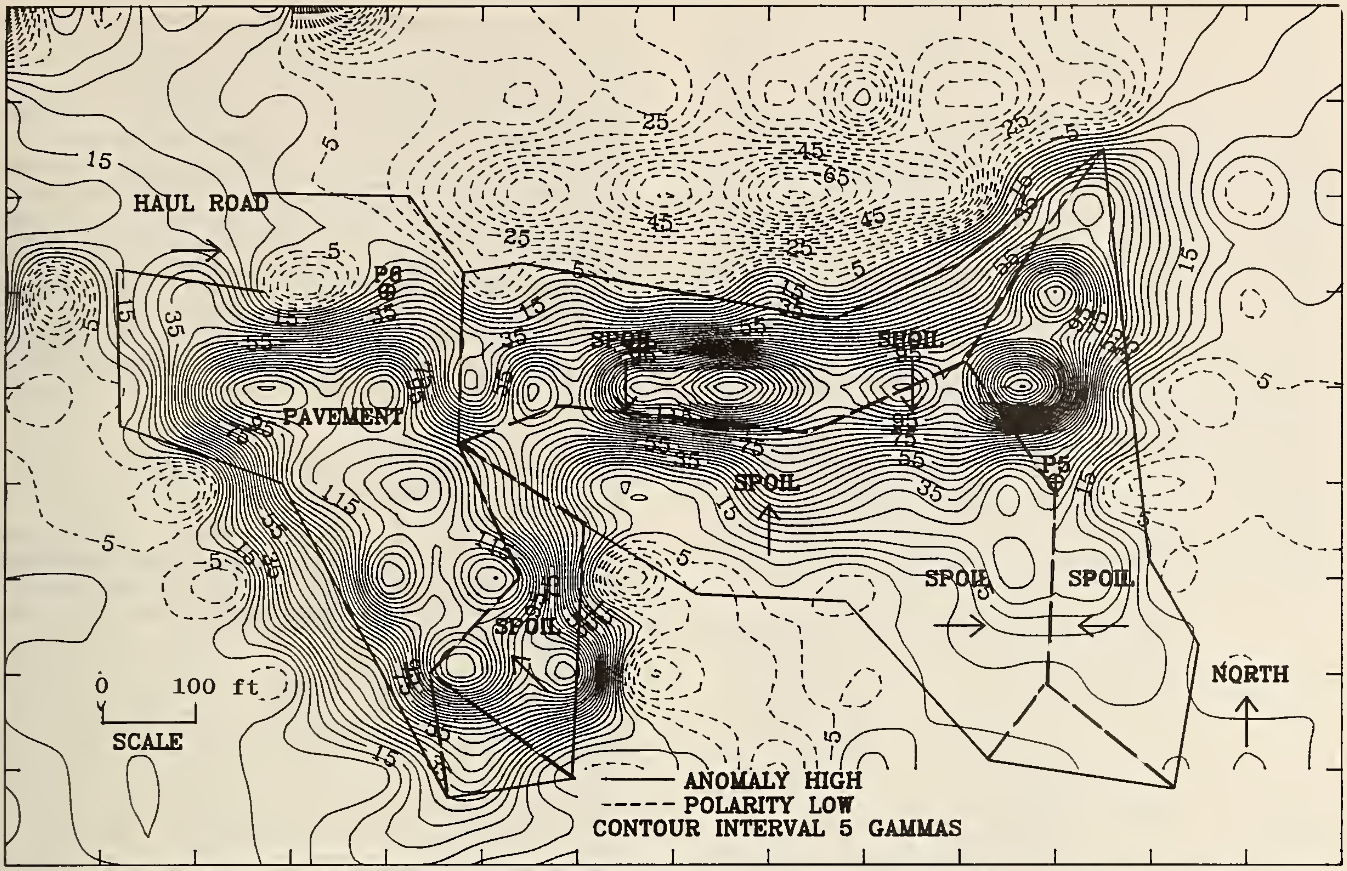


Figure 8. A enlargement of the pit located in the southeastern portion of SW1, figure 7, showing the correspondence between the magnetic contours and the pit geometry. The pit boundary is indicated by a solid bold line; the bottom of the pit is indicated by a bold dashed line. Prior to refuse disposal the coal pavement was exposed in the western portion of the pit and the western highwall was vertical. The central and eastern portions of the pit are formed by spoil piles joining in the center of the pit at the bottom.

interpreted as refuse using EM disappear when the magnetometer is used. EM could define the refuse more clearly had additional traverses been completed using different intercoil spacings and vertical as well as horizontal coplanar configurations. However, I was able to collect seven times as many data points with the magnetometer per man-hour of effort than with EM. Furthermore, one traverse is all that is needed with the magnetometer for quantitative interpretations, as opposed to two or four with EM. Thus, for good quantitative EM data it would be necessary to spend 28 man days in the field compared with one with the magnetometer. DC electrical resistivity profiling could have been used to provide electrical information similar to EM; note, however, that this technique is some three to six times more time consuming than EM (Ladwig 1982).

On the basis of theory, EM techniques must be expected to do poorly over magnetic targets. The apparent conductivity as measured by the electromagnetic terrain conductivity meter is defined as

$$\sigma_a = \frac{4}{w\mu_o s^2}\,\frac{H_s}{H_p}$$

where H_s = secondary magnetic field at the receiver coil
H_p = primary magnetic field at the receiver coil
$w = 2\pi f$
μ_o = permeability of free space
σ = ground conductivity (mho/m)
s = intercoil spacing (m)
f = frequency (Hz) (McNeill 1980)

The μ in this equation is usually taken as μ_o the permeability of free space under the assumption of nonmagnetic targets. For a magnetic target, μ is higher than μ_o, so the conductivity the instrument measures comes out lower than the true apparent conductivity. The fact that the target is magnetic actually degrades the EM measurement.

The mapping effort on SW1 clearly demonstrates the effectiveness of mapping refuse buried in pods with singular dimensions in the tens to hundreds of feet. A second site NW1 was mapped to determine the effectiveness of the magnetometer in mapping refuse buried in much smaller, widely scattered pods.

FIELD STUDY AT NW1 SITE

Site Description

In contrast to SW1, refuse disposal operations at NW1 occurred while the site was actively being mined. NW1 is a 40-acre site in Clarion County, Pa. The extreme western portion of the site was mined by a previous operator with perhaps only one or two crop line cuts being taken. The remainder of 40acre site was mined in 1971 and 1972. Reclamation was completed in 1973 (Ladwig 1982). No particular portion of the site was dedicated to refuse disposal; rather the refuse was simply dumped into any working pit that happened to be open at that time. Consequently only one or two truckloads make up the entire refuse pod in most locations. A typical coal dump truck has a capacity of about 25 cu yd. The resultant pods or piles would be no more than about 15-20 ft in the longest dimension.

Conductivity Field Work

A portion of NW1 was mapped in 1982 using EM by Ken Ladwig, formerly with the U.S. Bureau of Mines. Much of the remaining portion was mapped in 1984 using the same technique. The purpose of the mapping was to locate AMD and AMD sources. Buried tipple refuse is suspected as one of those sources. The EM mapping was completed using both 10- and 20-m intercoil separations with both horizontal and vertical coplanar dipole configurations. Readings were taken every 10 m along traverses approximately 25 m apart (Ladwig 1982).

Conductivity Survey Results and Interpretation

Figure 9 is typical of the conductivity contour maps produced from NW1. This figure covers the southeastern portion of NW1. Several large, steep

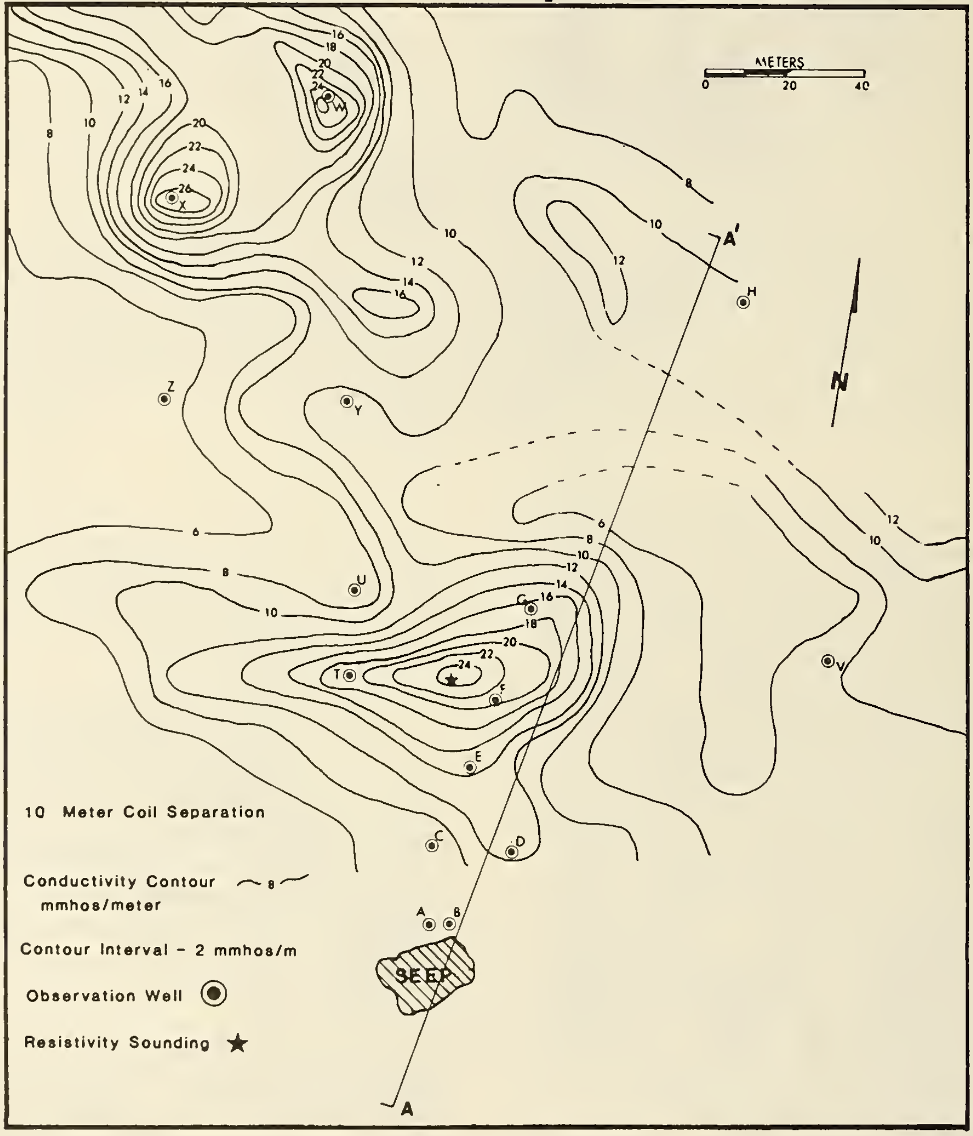


Figure 9. A typical terrain conductivity contour map resulting from Ladwig's work at NW1. The area represented is in the southeastern portion of the site. Conductivity highs represent AMD or AMD sources (Ladwig, 1982)

gradient anomalies were mapped at the site which Ladwig interpreted as signifying AMD or AMD sources. Without drilling, one cannot distinguish between anomalies that reflect AMD and those that reflect refuse. Several confirmation holes were drilled at the locations shown in figure 9. Only 2 holes, X and F, encountered refuse. Ladwig concluded that the anomalies were produced by a combination of both AMD and refuse (Ladwig 1982). In short, the EM work on this site demonstrates the similarity in electrical conductance properties between AMD and refuse as well as the difficulty in identifying either one with confidence.

Magnetometer Field Work

The entire 40-acre site was mapped in July 1987 using a magnetometer. Readings were initially taken on a 25 by 50 ft grid spacing. A contour plot of the readings is presented in figure 10. Due to resolution, only a 10-acre portion of the 40 acres is shown. At this rather coarse spacing, many isolated anomalous readings were observed. Consequently, to get more detail, additional traverse lines were added resulting in over half the site being mapped on a 25 by 25 ft or tighter grid. It should be noted that the area presented in figure 10 is located to the west of that presented in figure 9. Further, EM contours from Ladwig's second effort have been superimposed over figure 10 for comparison and later discussion.

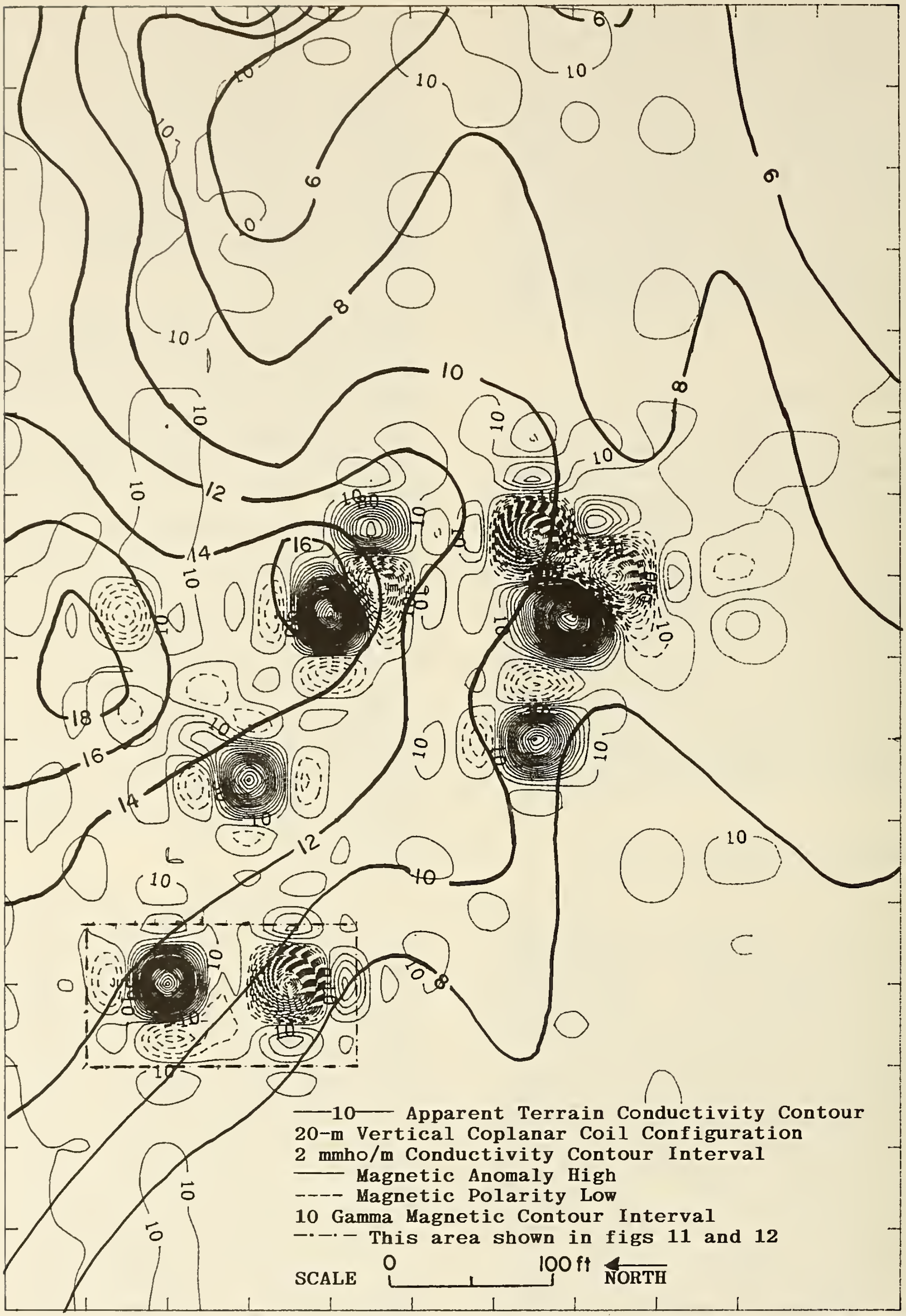
Magnetometer Survey Results and Interpretation

Many anomaly highs and polarity lows are observed in the magnetic anomaly map, figure 10. The positive anomalies are indicated by solid lines; the polarity lows as dashed lines. Both high and low anomalies are shaped like circles or rounded rectangles. Additionally, maximum anomaly amplitudes vary considerably, in part because of the grid spacing used. Most of the piles can be located, but not delineated because only a few data points define each anomaly. If the grid point where the reading is taken does not coincide with the point of maximum amplitude for the pile, readings of a few tens of gammas rather than a few hundred are commonly recorded. Closer grid spacing would be required to better define these anomalies, but wasn't deemed necessary. The 25 by 25 ft grid spacing was sufficient to locate the small isolated refuse piles.

Increased resolution through closer grid spacing is illustrated in figures 11 and 12. The anomaly to be redefined is the one located in the lower left portion of figure 10. The area in figure 11 is the result of mapping on a 25 by 25 ft grid. The appearance is that of a single source with the positive portion of the anomaly (solid lines) on the left and the polarity low (dashed lines) on the right with about a 50 ft separation. The area was remapped on a 5 by 5 ft grid as shown in figure 12. We find there are two sources, each consisting of probably a single truckload of refuse. The anomaly wavelength indicates a lateral dimension of about 15 ft. The steep contour gradient further indicates that the burial depth is shallow. A drill hole located over the anomaly on the right encountered refuse from 12.5 to 27.5 ft.

Additional confirmation of the presence of refuse was made through DC electrical resistivity soundings using the Schlumberger array. Soundings were taken over both positive magnetic anomalies as well as at locations beyond the anomalies. The soundings over the anomalies indicate low resistivity (high conductivity) zones. Soundings taken away from the anomalies indicated uniform, poorly conductive materials both near the surface and at depth. The presence of refuse beneath anomalies was confirmed at several other locations across the site using both air rotary drilling and DC electrical resistivity soundings. In contrast to the EM electrical methods, DC electrical techniques like Schlumberger soundings are not affected by unusual magnetic permeabilities. However, standard interpretation packages for Schlumberger soundings assume infinite flat layers rather than the compact local sources we know to be present here. Hence, at this location the Schlumberger DC results are useful quantitatively, but probably not qualitatively.

The presence of polarity lows of arbitrary amplitudes that are located in an arbitrary direction from the highs, figures 10 and 12, indicate that remanent magnetization resulting from spontaneous combustion is dominant in these source bodies. This further indicates that spontaneous combustion occurred in the refuse before it was trucked onto the site. Several facts need to be recalled: 1) the magnetic fraction of all samples from both NW1 and SW1 was minute, but comparable in volume 2) magnetic combustion particles were predominant at NW1, 3) remanent magnetization, a result of combustion, is often many times stronger than induced magnetization, and 4) if reoriented, remanent magnetization is independent of the local magnetic field. First, the size of refuse piles are orders of magnitude smaller at NW1 than at SW1, yet maximum anomaly amplitudes are twice as great at NW1. This indicates greater magnetic susceptibilities at NW1. Lastly, if induced magnetization were predominant, or if the spontaneous combustion occurred after the refuse had been dumped on the site, all resulting anomalies would be oriented north-south with the polarity lows to the north. Such is not the case here. Polarity lows do not exhibit a



—10— Apparent Terrain Conductivity Contour
20-m Vertical Coplanar Coil Configuration
2 mmho/m Conductivity Contour Interval
—— Magnetic Anomaly High
---- Magnetic Polarity Low
10 Gamma Magnetic Contour Interval
-·-·- This area shown in figs 11 and 12
SCALE
0
100 ft
NORTH
6
8
10
12
14
16
18

Figure 10. Superimposed magnetic and terrain conductivity maps of the SW 10-acres of NW1 site. Anomaly highs indicate the location of truckload sized pods of refuse buried at the site. Except for a few correspondences, detection of refuse by EM methods were poor. (Conductivity contours from Ladwig, 1984).

uniform north-south alignment. We infer from this that the source bodies came off the dump trucks in fairly large coherent blocks permitting the domains within the magnetic components to remain aligned.

Comparison of EM and Magnetometer Results

In figure 10 Ladwig's conductivity contours are superimposed over the magnetometer contours. Only a 10-acre

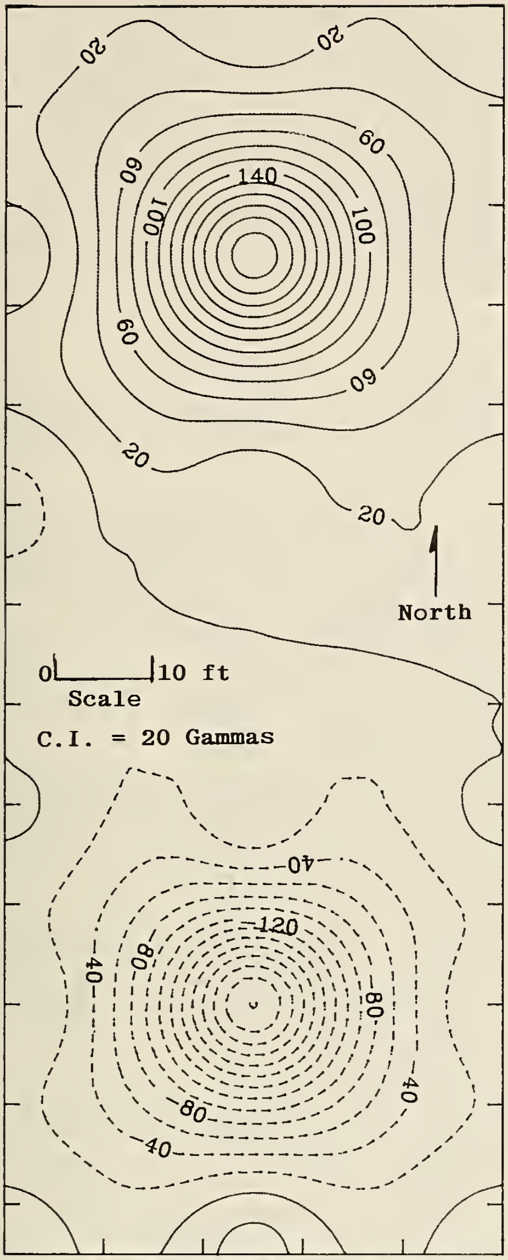

20
20
60
140
100
60
100
60
60
20
20
North
0
10 ft
Scale
C.I. = 20 Gammas
40
120
80
40
80
80
40
40

Figure 11. Magnetometer contours resulting from truckload sized pods of refuse mapped on a 25 by 25 ft grid. This appears as a single source body with the anomaly high to the north and the polarity low to the south.

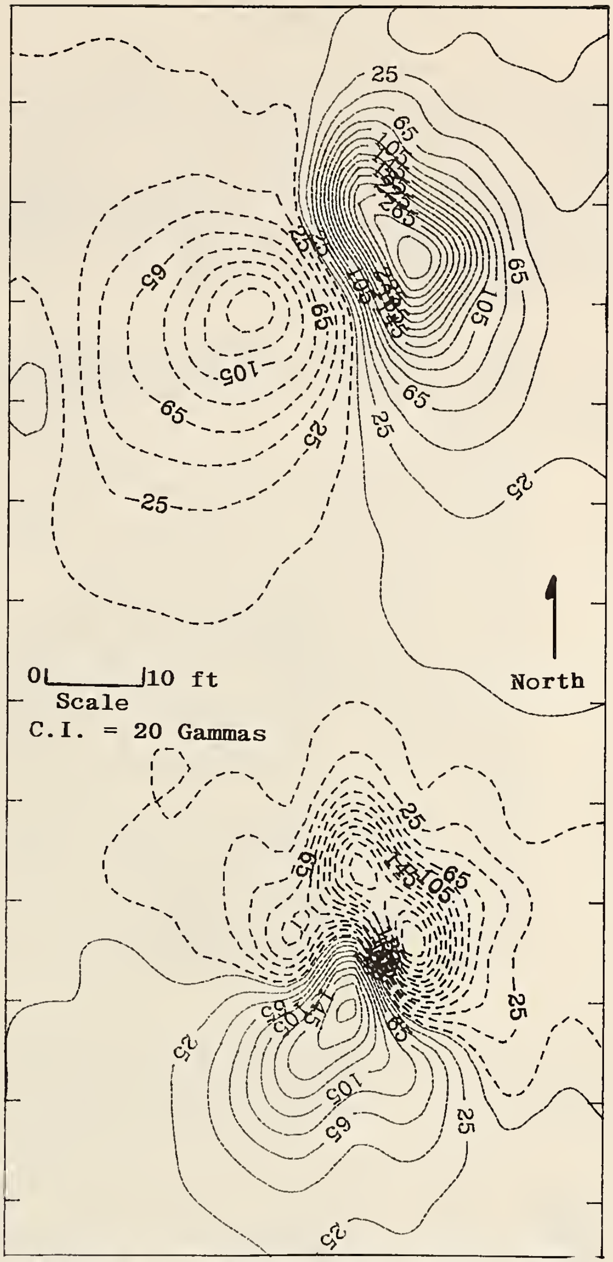

25
65
105
25
65
105
65
105
65
65
25
25
25
25
25
North
0
10 ft
Scale
C.I. = 20 Gammas
25
65
145
105
65
25
65
105
145
105
65
25
25
25

Figure 12. Magnetometer contour map resulting from mapping the area shown in Figure 11 on a 5 by 5 ft grid. Note the increased detail indicating the presence of two anomalies rather than just one.

portion of the 40-acre site is shown. Ladwig found a background conductivity value of 10 mmhos/m or less at this site (Ladwig 1982). An area of values greater than 10 mmhos/m is present in the left-central portion of the figure, implying possible AMD or AMD sources there. Note that several magnetic anomalies interpreted as refuse locations are present in this area. The 16 mmhos/m contour coincides with a magnetic anomaly, but there appears to be few further correspondences between the EM contours and the refuse pile locations as interpreted magnetically. Also, a number of refuse anomalies are mapped using magnetics further to the right where EM values are below 10 mmhos/m. Also the conductivity contours cut across the magnetic anomalies rather than surround them as would be expected.

Additional EM readings at much closer intervals would probably have identified more of the refuse locations. However, it may well be that the EM is more responsive to the AMD than to the refuse at this site, hence the conductivity may be showing an AMD pattern or the locations of nonmagnetic AMD sources.

CONCLUSIONS

The magnetometer's ability to clearly define buried refuse regardless of pod size makes it an effective geophysical tool in locating buried tipple refuse, a potential source of acid mine drainage. The property of remanent magnetism, which is somewhat unique to this particular type of refuse, allows the magnetometer to identify it against a background of mine spoil as well as AMD.

When attempting to map the locations of buried refuse, the magnetometer has many advantages over terrain conductivity. These include:

1) The location of the refuse is not masked by AMD or highly conductive spoil material as it is with EM.
2) Small piles of refuse, no larger than a single truckload are easily detected with the magnetometer.
3) Quantitative as well as qualitative determinations can be made with magnetometer data obtained from a single traverse of the area. A single traverse with EM provides qualitative data but multiple traverses are required before quantitative interpretations are made.
4) An area can be mapped from 7 to 28 times faster with the magnetometer than with EM for an equivalent amount of data.
5) Quantitative interpretations are easier and much quicker with the magnetometer than with EM.

Terrain conductivity has an advantage over the magnetometer, however. EM can detect AMD as well as structural features which the magnetometer cannot.

It was noted earlier that the refuse disposed of at both sites originated from tipples where magnetite was used. The ability of the magnetometer to detect refuse from plants which did not use magnetite is as yet unknown. Indications are, however, that the refuse may still be detected provided some degree of spontaneous combustion has taken place.

Selection of method in a particular investigation should be dictated by the purpose of the study. If refuse is to be mapped for the purpose of reprocessing then the magnetometer should be used. However, if the study is for delineating AMD and its sources, then a combination of both methods is suggested. Even though an area can be mapped more rapidly with the magnetometer, the total field time with either method is insignificant considering the wealth of information which can be collected.

ACKNOWLEDGMENTS

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THE USE OF PRE-AERATION TO REDUCE THE COST OF NEUTRALIZING ACID MINE DRAINAGE[1]

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Abstract.--Acid mine drainage (AMD) pumped from an underground mine can contain dissolved carbonates. When hydrated lime is added in the treatment process to neutralize the AMD, the dissolved carbonates react with the lime to form insoluble calcium carbonate. The presence of dissolved carbonates in the untreated water increases both the amount of lime required to neutralize the AMD and the amount of sludge formed during the treatment process. Laboratory tests show that dissolved carbonates can be removed as gaseous carbon dioxide by aerating the AMD prior to the addition of lime (pre-aeration). Field tests were conducted at three AMD treatment plants. The tests demonstrated that pre-aeration is an effective method of reducing treatment costs for an AMD containing dissolved carbonates. Pre-aeration has been permanently applied at each of the sites, and treatment costs have been substantially reduced, while strict compliance with environmental permits has been maintained. The chemistry of dissolved carbonates in the AMD treatment process, the results of the three field tests, and the specific modifications that were made to the treatment plants are discussed.

INTRODUCTION

Acid mine drainage (AMD) is formed by the weathering of pyritic materials, predominantly FeS_2, that are present in the waste found in strip mine spoil, coal refuse piles, etc., as well as from exposed pyritic surfaces in active and abandoned underground mines. These pyritic materials are oxidized in the presence of air (oxygen), water, and certain bacteria to yield large quantities of iron, sulfate, and acidity (Reaction 1), according to Stumm and Morgan (1981).

$$FeS_2(s) + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + H_2SO_4 + SO_4^{2-} \qquad (1)$$

Sulfuric acid, one product of the oxidation reaction, is readily recognizable as an acid. The ferrous iron produced in Reaction 1 is also a source of acidity as shown in Reactions 2 and 3 (Stumm and Morgan, 1981). The abiotic oxidation of ferrous iron (Reaction 2) proceeds slowly in acidic solution. In the absence of significant bacterial activity the acidity associated with ferrous iron in many deep mine sites is not released until the water is pumped to the surface for treatment.

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \qquad (2)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \qquad (3)$$

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of the Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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The water entering a deep mine does so by percolating through the overburden and surrounding strata. If the water passes through limestone, it will contain alkalinity in the form of calcium carbonate and/or bicarbonate when it enters the mine (Parizek and Tarr, 1972). When water containing alkalinity encounters the products of pyrite oxidation, neutralization takes place (Reactions 4 and 5).

$$H_2SO_4 + 2\ CaCO_3 \rightarrow Ca^{2+} + SO_4^{=} + Ca(HCO_3)_2 \qquad (4)$$

$$H_2SO_4 + Ca(HCO_3)_2 \rightarrow Ca^{2+} + SO_4^{=} + 2\ H_2CO_3 \qquad (5)$$

This neutralization moderates the pH of the AMD by consuming sulfuric acid and may limit the solubility of ferrous iron. However, the products of this neutralization, bicarbonate ion and carbonic acid, are weak acids. When AMD that has been partially neutralized in this fashion is pumped to the surface and treated with an alkaline material such as hydrated lime, the carbonic acid and bicarbonate ion react with the lime to form sparingly soluble calcium carbonate (Reactions 6 and 7). Because of these reactions, excessive amounts of alkaline material must be used to achieve a pH that is favorable for ferrous iron oxidation and manganese removal.

$$H_2CO_3 + Ca(OH)_2 \rightarrow \underline{CaCO_3}\downarrow + 2\ H_2O \qquad (6)$$

$$2\ HCO_3^{-} + Ca(OH)_2 + Ca^{2+} \rightarrow 2\ \underline{CaCO_3}\downarrow + 2\ H_2O \qquad (7)$$

Work performed in our laboratory demonstrates that the AMD pumped from most deep mines contains dissolved carbonates which can be removed from solution as gaseous carbon dioxide. The removal is accomplished by aerating the mine water prior to the addition of alkaline material (pre-aeration) and can result in a substantial reduction in the amount of alkaline material required for neutralization. The use of pre-aeration to reduce AMD treatment costs has been reported previously (Herman and Korb) for a mine drainage which was treated to a high pH (>10) to assure manganese removal. Our work indicates that pre-aeration is much more broadly applicable than previously reported.

Field Test

An AMD treatment plant located in western Pennsylvania was used to investigate the utility of pre-aeration. At this site (fig. 1), AMD containing 520 mg/L of dissolved carbonate (calculated as CO_2) is pumped from a flooded deep mine. A side stream is split from the main flow and is used to form a lime slurry. The slurry stream is recombined with the main flow of AMD in an open channel which leads to a series of two aeration basins.

In the first basin an aerator mixes the lime slurry with the main flow of AMD and initiates the ferrous to ferric iron oxidation reaction. In the second basin, aerators drive the oxidation reaction almost to completion.

The treated water discharges from the second aeration basin through an open channel into a large settling basin. Here, continued oxidation takes place, and the insoluble ferric oxyhydroxide sludge settles out. Clarified water discharges from the settling basin, and the solids are pumped from the bottom of the settling basin back into the mine.

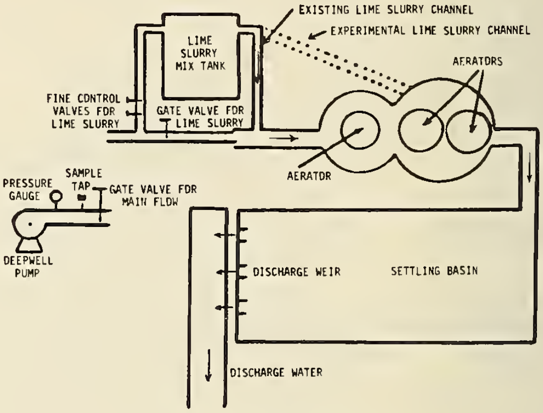


Figure 1.--Sketch of Site 1.

The field test consisted of a baseline test in which the plant was operated normally. A six-day pre-aeration test was then performed. The AMD was treated at the same flow rate and same pH (8.4) as the baseline test. Pre-aeration was accomplished by diverting the lime slurry to the second aeration basin (fig. 1). In this configuration the first basin was used to pre-aerate the unlimed AMD causing dissolved carbon dioxide to evolve to the atmosphere. Even though the residence time (~15 minutes) in the pre-aeration basin was too short for optimum removal of the dissolved carbonates, pre-aeration produced the following results:

- 38% of the dissolved carbonates were removed in the pre-aeration basin.
- Hydrated lime use was reduced 27%.
- The concentration of unreacted ferrous iron leaving the aeration basin was reduced from 55 mg/L to 5 mg/L.
- The sludge settling rate improved dramatically, and the sludge volume was reduced by about 50% (fig. 2).
- The discharge water quality was maintained with the concentration of total iron <2 mg/L and manganese <1 mg/L.

The treatment plant continued to operate as it was configured for the experiment for the next 18 months. As a result treatment costs were reduced by approximately $300,000/yr.

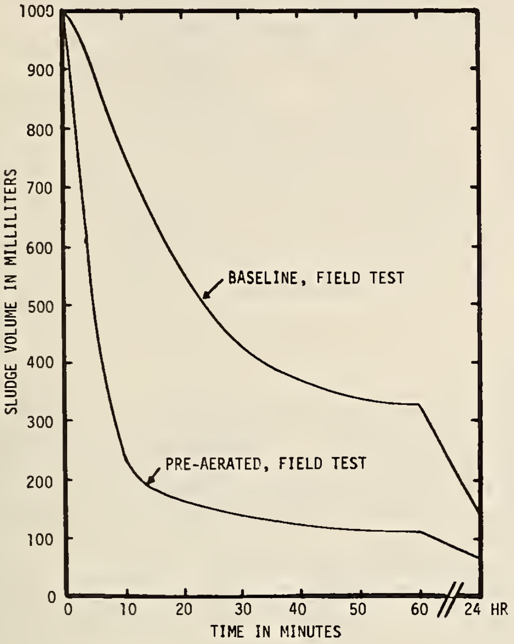
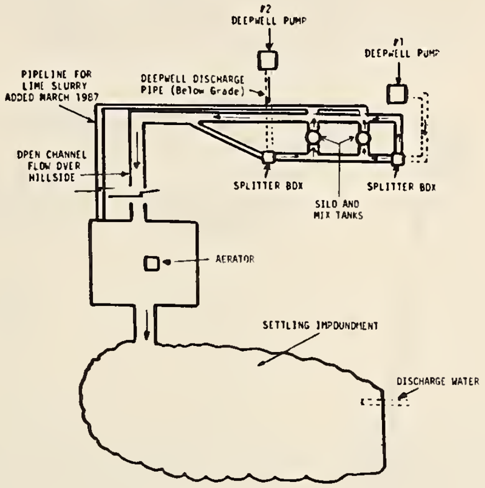


Figure 2.--Sludge Settling Data for Site 1.

Recently, the treatment plant was modified, and a permanent pre-aeration basin was constructed. Based on two weeks of operating data, chemical costs for the new plant are 62% less than the costs before pre-aeration (table 1). Approximately one-fourth of the savings is due to improved water quality in the flooded mine. One-half of the savings is due to preaeration. The remaining one-fourth is due to improved lime utilization.

Application to Other Sites

Field tests and modifications were made at two additional sites. At one of these sites (Site 2 shown in fig. 3) the treatment plant was built on a hillside with the lime handling equipment and mix tanks at a higher elevation than the aeration basin, which was at the base of the hill. The treatment plant was designed as previously described (Site 1) with a small side stream split off to form a lime slurry and then recombined with the main AMD flow.



#2
DEEPWELL PUMP
#1
DEEPWELL PUMP
PIPELINE FOR
LIME SLURRY
ADDED MARCH 1987
DEEPWELL DISCHARGE
PIPE (Below Grade)
OPEN CHANNEL
FLOW OVER
HILLSIDE
SPLITTER BOX
SPLITTER BOX
SILO AND
MIX TANKS
AERATOR
SETTLING IMPOUNDMENT
DISCHARGE WATER

Figure 3.--Sketch of Site 2.

The AMD treated at this site has a pH of 4.6 and contains 200 mg/L of dissolved carbonates (table 2). Laboratory tests indicated, because of the low pH of the AMD, that the dissolved carbonate removal at this site would be rapid. Instead of installing a pre-aeration basin, it was decided to utilize the site topography. A pipeline was installed to transport the lime slurry to the aeration basin. The bulk of the AMD was allowed to flow over

Table 1.--Analysis of Site 1 AMD and the Effect of Pre-aeration.

AMD Sample	pH	Fe^{2+} (mg/L)	Total Dissolved Carbonates (mg CO_2/L)	Lime Requirement (ton/MM gal)
January 1986				
Raw	6.0	603	512	8.31
Pre-aerated	6.4	585	317	6.03
August 1987				
Raw	6.2	447	524	5.76(1)
Pre-aerated	6.5	368	189	3.19

(1) Theoretical value calculated from the concentration of ferrous ion and dissolved carbonates measured in the raw AMD.

the hillside in a rock-lined, open channel. The turbulent flow of the acid water resulted in almost complete removal of the dissolved carbonates.

The plant has continued to operate with pre-aeration for approximately 7 months. The use of pre-aeration at this site reduced lime use by approximately 40% and resulted in a modest improvement in sludge settling rate (fig. 4) and sludge volume. Treatment costs at this site could be further reduced by moving the lime handling equipment to the base of the hill next to the aeration basin. This would allow all the AMD to be pre-aerated in the open channel before contacting lime.

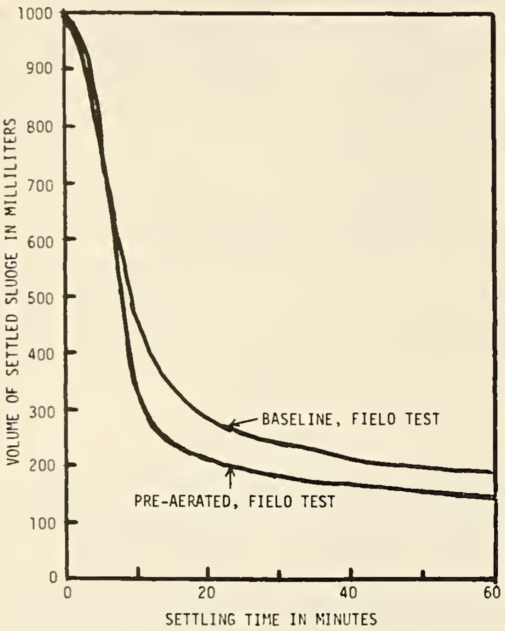


Figure 4.--Sludge Settling Data for Site 2.

At a third site, pre-aeration was accomplished by installing an aerator in an existing AMD holding pond (fig. 5). This pond was initially included in the treatment plant design to allow AMD, which is pumped to the plant from three different sources, to mix and equilibrate prior to treatment (table 3). The pond is an ideal site to retrofit a pre-aerator. Pre-aeration removes approximately 60% of the dissolved carbonates at this site, and the quantity of alkaline material used at the plant has been reduced by more than 50%.

DISCUSSION OF RESULTS

The chemical mechanism for the removal of dissolved carbonates can be explained as follows. Carbonic acid, one of the products of the reaction of calcium carbonate and sulfuric acid, exists in an acidic solution as a component of two chemical equilibria (Reactions 8 and 9).

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \qquad (8)$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_2(aq) \qquad (9)$$

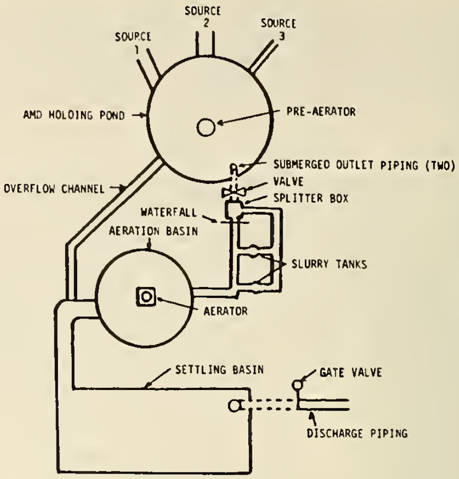


Figure 5.--Sketch of Site 3.

The chemical reactions of these equilibria provide a pathway for converting bicarbonate ion to carbonic acid and ultimately for converting carbonic acid to dissolved carbon dioxide. Carbon dioxide has a very limited solubility (<1 mg/L) in an aqueous solution that is in equilibrium with the atmosphere (Cole, 1979). Aerating an acidic solution that contains dissolved carbonates causes carbon dioxide to be stripped from solution. This shifts the equilibria of Reactions 8 and 9, and more carbon dioxide is formed as the solution equilibria are re-established. In theory, carbon dioxide removal can continue in this manner until the dissolved carbonate concentration is <1 mg/L. In practice, complete removal of the dissolved carbonates is unlikely, and the pH of the untreated AMD determines how difficult carbonate removal will be.

As indicated above, prior to reaching equilibrium with atmospheric CO_2, the relative concentrations of the various carbonate species in AMD are governed by the equilibria of Reactions 8 and 9. The equilibrium of Reaction 9 lies far to the right, indicating that associated carbonic acid is always a minor component of the carbonate system (Cotton and Wilkinson, 1972). The equilibrium of Reaction 8 indicates that in strongly acidic solution (pH <4.5) dissolved carbon dioxide is the only significant carbonate species. At more moderate pH values (pH >6.4) bicarbonate ion becomes the predominate species.

The form of the carbonates in an AMD is critical to the design of a pre-aeration system because dissolved carbon dioxide is readily stripped from solution, but bicarbonate ion is not. In order to remove bicarbonate from solution the bicarbonate ion must react to form carbonic acid (Reaction 10) and then dissociate to dissolved carbon dioxide (Reaction 11). This sequence of reactions takes time, particularly Reaction 11 (Cotton and Wilkinson, 1972).

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \qquad (10)$$

Table 2.--Analysis of Site 2 AMD and the Effect of Pre-aeration.

Sample	Flow Rate (gal/min)	pH	Total Iron (mg/L)	Dissolved Carbonates (mg CO_2/L)	Lime Requirement (ton/MM gal)
Pump #1	1,250	4.5	206	190	2.7
Pump #2	1,500	4.6	164	207	2.5(1)
Combined AMD After Pre-aeration	2,750	4.8	180	3	1.6

(1) Theoretical value calculated from the concentration of ferrous ion and dissolved carbon dioxide in the raw AMD.

Table 3.--Analysis of Site 3 AMD and the Effect of Pre-aeration.

AMD Sample	pH	Fe^{2+} (mg/L)	Dissolved Carbonates (mg CO_2/L)	Lime Requirement (ton/MM gal)
Composite				
Raw	6.4	306	546	3
After Pre-aeration	6.6	266	233	1.7

$$H_2CO_3 \rightarrow CO_2(aq) + H_2O \qquad (11)$$

This pH dependent distribution of the carbonate species and the time required to remove the bicarbonate ion explains the differences in the performance of the three pre-aeration systems that were discussed. At Site 2, where AMD of pH 4.6 is treated, the carbonates are present as dissolved carbon dioxide, a rapid and nearly complete removal of the carbonates is accomplished by simply allowing the water to fall over a hillside. At Site 1, where AMD of pH 6.2 is treated, approximately half of the dissolved carbonates are present as bicarbonate. Agitating this water in a large basin with mechanical aerators removes only 65% of the carbonates. At Site 3 the pH of the water is also high (6.4), and only partial removal of the dissolved carbonates is achieved.

An additional point worth mentioning is that for some mine drainages, pre-aeration alone can effect neutralization and iron removal. For mine drainages where the molar ratio of bicarbonate ion to ferrous ion exceeds 2:1, the acid produced by iron oxidation (Reactions 2 and 3) is consumed by the conversion of bicarbonate ion to carbon dioxide (Reactions 10 and 11). Since this condition (high bicarbonate concentration) can only occur when the pH of the untreated water is high (>6), pre-aeration can cause the iron to oxidize and precipitate while the pH remains at a level that is suitable for discharge.

SUMMARY

Pre-aeration has proven to be a very effective means of treatment cost reduction for deep mine AMD. In addition to the three sites discussed in this paper, pre-aeration has recently been installed at one other site and has been recommended for several others. It is anticipated that pre-aeration will eventually reduce AMD treatment costs for Consolidation Coal Company by approximately one million dollars per year.

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METHODS FOR DETERMINING FUNDAMENTAL CHEMICAL DIFFERENCES BETWEEN IRON DISULFIDES FROM DIFFERENT GEOLOGIC PROVENANCES[1]

Richard W. Hammack,[2] Ralph W. Lai,[3] and J. Rodney Diehl[3]

Abstract.--X-ray photoelectron spectroscopy (XPS), evolved gas analysis (EGA), and froth flotation tests were used to compare iron disulfides of hydrothermal, sedimentary/hydrothermal, and sedimentary origin. A specimen composed of equal amounts of pyrite and marcasite was also evaluated. The susceptability of iron disulfide surfaces to oxidation was measured using XPS and EGA techniques. XPS analyses indicated the following order of increasing oxidation rate at 21 pct oxygen and 88 pct relative humidity: sedimentary/hydrothermal pyrite (0.70 mg SO_4^{-2}/hr per gram of FeS_2)< hydrothermal pyrite (0.83 mg SO_4^{-2}/hr per gram of FeS_2)< hydrothermal pyrite/marcasite (1.34 mg SO_{4-2}/hr per gram of FeS_2)< sedimentary pyrite (3.53 mg SO_4^{-2}/hr per gram of FeS_2). Oxidation rates measured by XPS are based solely on the sulfate/sulfide ratios at the surface, where oxidation is not inhibited by mass transfer limitations. Therefore, these rates are much higher than previously published rates based on bulk iron disulfide content. The comparison of EGA results with oxidation rates measured by XPS showed that for sedimentary pyrites, higher temperatures of SO_2 evolution corresponded to lower oxidation rates. Weathering rates for hydrothermal iron disulfides appear to be independent of SO_2 evolution temperatures. In flotation tests with an anionic fluorosurfactant collector, hydrothermal pyrite floated and sedimentary pyrite was depressed. Hydrothermal pyrite floated because it developed a positive surface charge in solution that allowed the attachment of the anionic collector. The negative charge developed by sedimentary pyrite in this solution repelled the anionic collector, depressing sedimentary pyrite. This research provides a better understanding of iron disulfide oxidation and illustrates inherent differences in physical and chemical properties that significantly alter the behavior of pyrites of different geologic provenance.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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INTRODUCTION

The weathering of sulfide minerals accounts for most of the surface water and groundwater contamination that results from mining. Pyrite, the most prevalent sulfide mineral, is primarily responsible for the acid discharges from underground coal and metal mines, surface mine spoils, and tailings (refuse) disposal areas. In general, not all pyrites weather at the same rate. This fact is apparent to anyone who has compared unweathered pyrite from a 50-year-old metal mine dump with pyrite from coal refuse that becomes encrusted with hydrated iron sulfates and oxyhydroxides (pyrite weathering products) in a matter of days. The rate at which pyrites oxidize varies significantly with surface area; many authors (Pugh and others, 1981; Pugh and others, 1984; and Nicholson and others, 1987) have shown that there is a positive, linear correlation between surface area and the rate of pyrite oxidation. Pyrites of sedimentary (low-temperature) origin typically display greater surface area, due to smaller mean particle size and greater surface irregularity, than pyrites of hydrothermal (high-temperature) origin. Therefore, sedimentary pyrite would be expected to be more reactive than hydrothermal pyrite. However, recent work (Esposito and others, 1987) has suggested that differences in surface area do not adequately explain differences in pyrite solubility.

In this study, pyrites of three different origins (sedimentary, sedimentary/hydrothermal, and hydrothermal) were compared, using x-ray photoelectron spectroscopy (XPS) weathering tests, evolved gas analysis (EGA), and flotation response measurements. A hydrothermal specimen containing about equal amounts of pyrite and marcasite was also evaluated. The intent of this study was to determine if surface area differences are solely responsible for the wide range of observed pyrite reactivities, or if fundamental chemical differences must also be considered. We also wished to determine if a simple analytical technique, such as EGA, could be used to quickly predict the rate at which different pyrites oxidize.

TECHNICAL APPROACH

XPS Weathering Tests

The intention was to measure only oxidation on the surface of iron disulfide particles where mass transfer effects are minimized. By minimizing mass transfer or diffusional effects, we hoped to measure rates that more accurately reflect the chemical kinetics of iron disulfide oxidation. Because rates measured in this study are based on the amount of iron disulfide at the surface and "available" for reaction, these rates are significantly faster (10 to 20 times) than rates typically reported for iron disulfide oxidation. Previous studies have based observed oxidation rates on bulk pyrite content (amount of sulfate produced or oxygen consumed per gram of bulk pyrite per hour), although only a small fraction of the bulk pyrite was at the surface and available for reaction. Available pyrite can be calculated from the bulk pyrite content, using surface area estimation or gas absorption techniques, but this calculation involves several approximations and can only be regarded as an estimate.

In contrast to previous studies, a surface analysis technique (XPS) that detects both pyritic sulfur and sulfate sulfur at the point of reaction was used. XPS provides quantitative elemental information with a detection limit of approximately 1 pct of atoms comprising the outermost monolayer. Different formal oxidation states can be distinguished, based on chemical shift information. Chemical shifts in the sulfur (2p) electron binding energy (fig. 1) were used in this study to distinguish between pyritic sulfur (reactant) and sulfate sulfur (product). The XPS analysis depth for pyrite is estimated to be about 2.3 nm, based on measured inelastic mean free paths for similar semiconductors (Buckley and others, 1987). This depth corresponds to the thickness of 4.24 pyrite unit cells (0.54175 nm/unit cell).

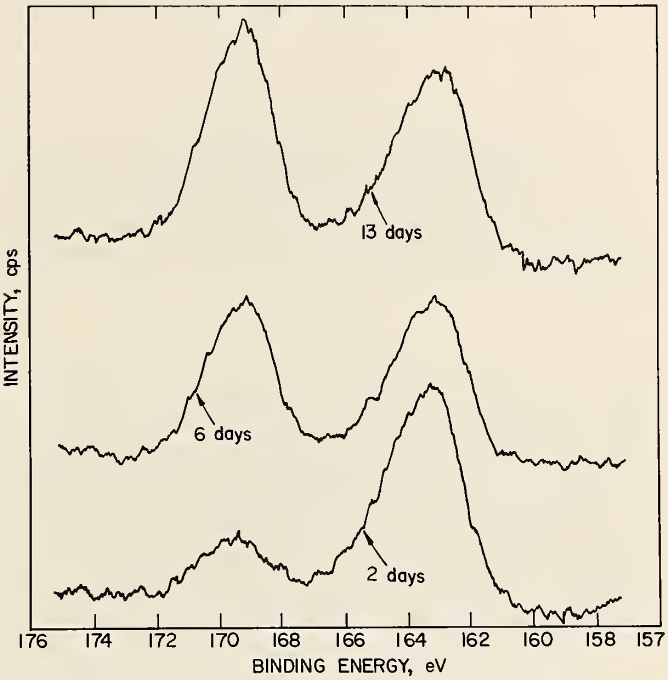

Figure 1. XPS SCAN of the sulfur (2p) region showing pyritic sulfur (B.E. = 163.5eV) and sulfate sulfur (B.E. =169.5eV) after 2, 6, and 13 days weathering.

Most published studies (Braley, 1960; Clark, 1965; Rogowski and Pionke, 1984; and Nicholson and others, 1987) have used sulfate production as a measure of the amount of oxidation that has taken place. In these studies, sulfate cannot be detected until it is dissolved and leached from the sample. This adds the complexity of sulfate solubility, pH-dependent sulfate adsorption, and sulfate transport considerations. Oxidation rates based on insitu detection of "available" pyrite and sulfate are better than rates based on "bulk" pyrite and leached sulfate for determining the mechanism and kinetics of pyrite oxidation. Because oxidation products were not leached from pyrite surfaces, the XPS technique permitted us to monitor, for the first time, the response of the oxidation rate to the accumulation of oxidation products.

Iron disulfides were weathered at a constant humidity of 88, pct but at different oxygen partial pressures. The conversion of sulfide sulfur to sulfate sulfur was monitored. For each sample, a percent conversion was calculated from the integrated photoelectron intensities for sulfate sulfur (binding energy = 169 eV) and pyritic sulfur (binding energy = 163 eV):

$$\text{Percent conv.} = \frac{\text{I sulfate sulfur}}{(\text{I sulfate sulfur} + \text{I sulfide sulfur})} \times 100 \text{ pct.}$$

where I = integrated photoelectron intensity.

Because sulfate sulfur and sulfide sulfur were the only observed sulfur species, the equation can be rewritten.

$$\text{Percent conv.} = \frac{\text{I sulfate sulfur}}{\text{I total sulfur}} \times 100 \text{ pct}$$

Evolved Gas Analysis

Evolved gas analysis is a thermal analysis technique that employs a programmable tube furnace to heat samples in an oxidizing atmosphere. The concentrations of gases evolved from the sample are monitored with respect to sample temperature. This study monitored the sulfur dioxide evolved from the high-temperature, anhydrous oxidation of iron disulfides:

$$2\ FeS_2 + 5.5\ O_2 \longrightarrow Fe_2O_3 + 4\ SO_2$$

Reactive iron disulfides are expected to oxidize and evolve sulfur dioxide at lower temperatures (lower activation energy) than more stable forms. Therefore, the sulfur dioxide evolution temperature can serve as a qualitative indicator of oxidation rate. EGA can rank iron disulfides in order of increasing reactivity by the anhydrous oxidation pathway but the correlation of sulfur dioxide evolution temperatures to hydrous, room temperature oxidation rates had not been established prior to this study.

SAMPLE DESCRIPTION

Pyrites from three different origins were tested in this study: a hydrothermal pyrite from Rico, Colorado; a pyrite of sedimentary origin that was later metamorphosed (sedimentary/hydrothermal pyrite) from the Mammoth anthracite seam in eastern Pennsylvania; and a sedimentary pyrite from the Upper Freeport coalbed, Coshocton County, Ohio. The hydrothermal pyrite/marcasite was from Joplin, Missouri. Additional iron disulfide samples that were not subjected to all tests included: sedimentary pyrites from the Pittsburgh coalbed, Barbour County, West Virginia (one sample) and from carbonaceous shales overlying the Clarion coalbed, Clearfield County, Pennsylvania (two samples); a hydrothermal pyrite from the Noranda Mine, Quebec, Canada; and a hydrothermal marcasite from Joplin, Missouri. Each sample for XPS and EGA analysis was crushed to a -150 to +200-mesh size fraction and centrifuged in acetyl tetrabromide (2.96 specific gravity) at 1500 rpm for 20 minutes to separate the iron disulfide from less dense clays, coal, and accessory minerals. The sink fraction was then washed with certigrav (1.20 specific gravity) to remove residual bromine. X-ray diffraction of the cleaned iron disulfides indicated that some mineral contaminants remained. These contaminants are listed in Table 1.

TEST PROCEDURES

XPS Weathering Tests

Immediately prior to weathering, samples for XPS analysis were washed with boiling 4.8 N HCl to remove sulfate, rinsed with methanol, and dried under vacuum. For each sample, thirty cylindrical wafers (13 mm diameter by 0.5 mm) were pressed under 700 kg/cm^2 pressure. Ten wafers of each sample were weathered simultaneously under the same conditions. Atmospheres used for this study contained 5, 10, and 21 pct oxygen (balance, nitrogen) at 88 pct relative humidity. Weathering chambers (fig. 2) were constructed so that wafers could be removed without disturbing or contaminating the atmosphere within the chamber. A total of three chambers were used so that samples could be weathered under all three atmospheres, simultaneously. Prior to each experiment, the chambers were washed with an acidified surfactant (sodium lauryl sulfate) solution and then rinsed with methanol to reduce the likelihood of bacterial catalysis. Periodically during the test, one wafer from each rod was removed from the chamber and placed in a Leybold-Heraeus LHS-10 photoelectron spectrometer operated at a pressure of 2X10^{-8} mbar or lower. X-rays from a magnesium anode (MgKα = 1253.6 eV) and an analyzer pass energy of 100 eV were used for the acquisition of S(2p) and Fe(2p) spectra. Binding energy calibrations were carried out by adjusting the measured binding energy for the C(1s) spectrum of adventitious carbon to 284.6 eV and shifting all other measured binding energies correspondingly. Peak areas within the S(2p) region attributable to sulfide sulfur and sulfate sulfur were determined with the Leybold-Heraeus DS-5 data system. The percent conversion was calculated for each wafer and plotted versus weathering time.

Table 1.--Mineral contaminants in iron disulfide samples.

Iron Disulfide	Mineral Contaminant(s)
Hydrothermal pyrite	Calcite
Sedimentary/ hydrothermal pyrite	Kaolinite, calcite, quartz, and dolomite
Sedimentary pyrite	Kaolinite, quartz, calcite, and marcasite
Hydrothermal pyrite/ marcasite	Quartz

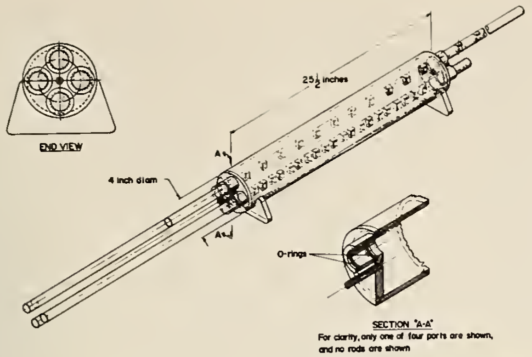
END VIEW
25½ inches
A
4 inch diam
A
O-rings
SECTION 'A-A'
For clarity, only one of four ports are shown, and no rods are shown

Figure 2. Schematic of weathering chamber used in this study.

EGA Tests

An instrument designed specifically for evolved gas analysis was used. This instrument (fig. 3) is similar to an evolved gas instrument constructed by LaCount and others (1983). Major components include an electronic mass flow controller/gas blender, a programmable tube furnace, a quadrupole mass spectrometer, a programmable analog to digital (A/D) converter, and a microcomputer.

The electronic mass flow controller/gas blender can provide selectable flow rates from 0.1 to 200 mL/min. It can also provide two-component gas mixtures ranging from 0.1 to 99.9 percent. In this study, a 10.0 percent oxygen/90.0 percent nitrogen mixture was introduced into the tube furnace at a flow rate of 100 mL/min.

Fifty milligrams of sample was diluted with 3g of tungsten oxide to insure uniform heating. The sample was then placed in a 2.54 cm diameter by 50 cm long quartz tube and secured with either glass wool or quartz wool, depending upon the maximum test temperature. A 32 mm (1/8 in), Type K thermocouple was inserted into the sample and the tube then placed in the furnace. Output from the thermocouple was conditioned by a linearizer and then passed to an A/D converter.

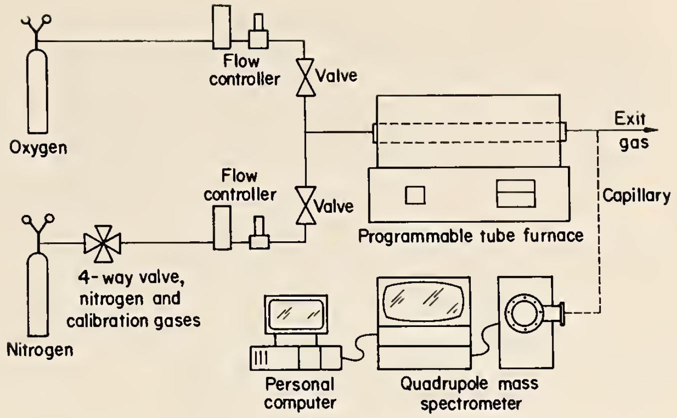
Oxygen
Flow controller
Valve
Exit gas
Flow controller
Valve
Capillary
Programmable tube furnace
4-way valve, nitrogen and calibration gases
Nitrogen
Personal computer
Quadrupole mass spectrometer

Figure 3. Schematic of evolved gas analysis instrument.

The tube furnace used was capable of performing two heating ramps with selectable heating rates, dwell temperatures, and dwell times. Starting at about 70°C, the sample was heated at a rate of 6°C/min up to 380°C. The heating rate was then decreased to 3°C/min up to 720°C, where each run was terminated.

Evolved gases were detected with a quadrupole mass spectrometer. The capillary inlet to the spectrometer was placed immediately downstream from the sample to minimize lag time between gas evolution and detection. The mass spectrometer was capable of simultaneously monitoring the ion current at 12 user-selected mass to charge ratios (M/e), although only the ion current at the M/e ratio of sulfur dioxide (64) is of interest here. This ion current was converted to partial pressure by multiplying by the calibration factor for sulfur dioxide. The partial pressure of sulfur dioxide and sample temperature were transmitted to a microcomputer where the data were converted to ASCII files and written to floppy disk. Commercially available graphics, gaussian peak fitting, and integration software were used to manipulate data.

Table 2.--Surface oxidation rates of iron disulfides at 88 pct relative humidity and 5 pct, 10 pct, and 21 pct oxygen.

	Oxidation Rate ($mg\ SO_4^{-2}\ g^{-1}\ FeS_2\ hr^{-1}$)		
Sample	5 pct O_2	10 pct O_2	21 pct O_2
Sedimentary pyrite	1.85	N.D.[1]	3.54
Hydrothermal pyrite/ marcasite	0.92	1.03	1.33
Hydrothermal pyrite	0.78	0.88	0.83
Sedimentary/ hydrothermal pyrite	0.41	0.54	0.70

[1] Not Determined--insufficient number of samples.

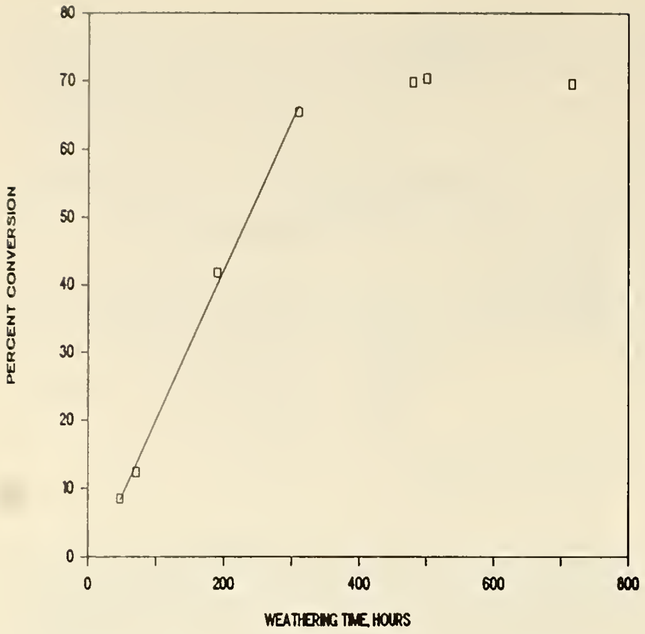

Figure 4. XPS monitored weathering of sedimentary pyrite at 21 pct. oxygen and 88 pct. relative humidity. Solid line denotes the least squares regression line used for rate calculations.

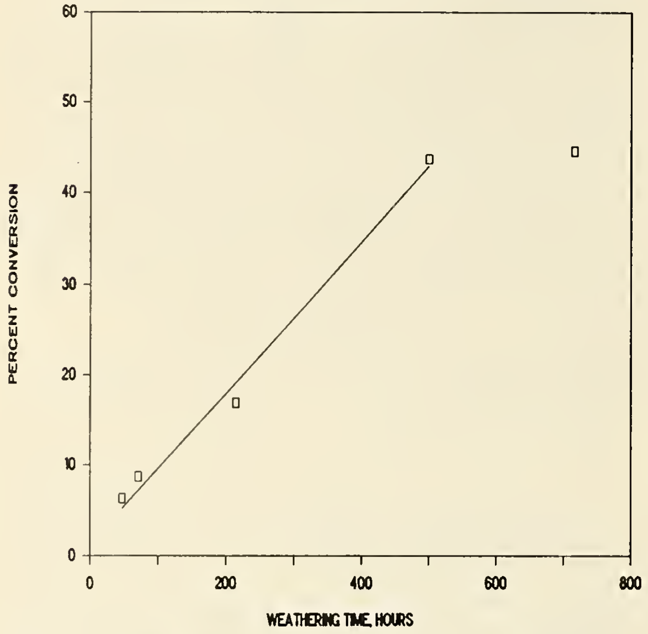

Figure 5. XPS monitored weathering of pyrite/ marcasite at 21 pct. oxygen and 88 pct. relative humidity. Solid line denotes the squares regression line used for rate calculations.

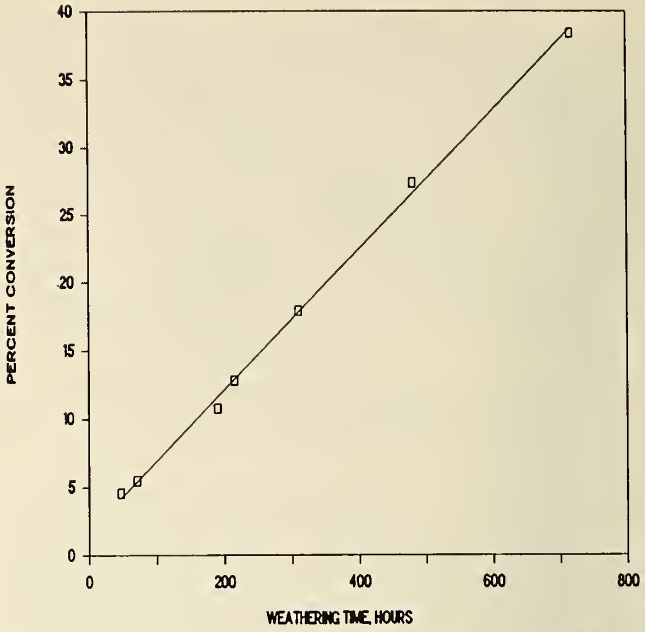

Figure 6. XPS monitored weathering of hydrothermal pyrite at 21 pct. oxygen and 88 pct. relative humidity. Solid line denotes the least squares regression line used for rate calculations.

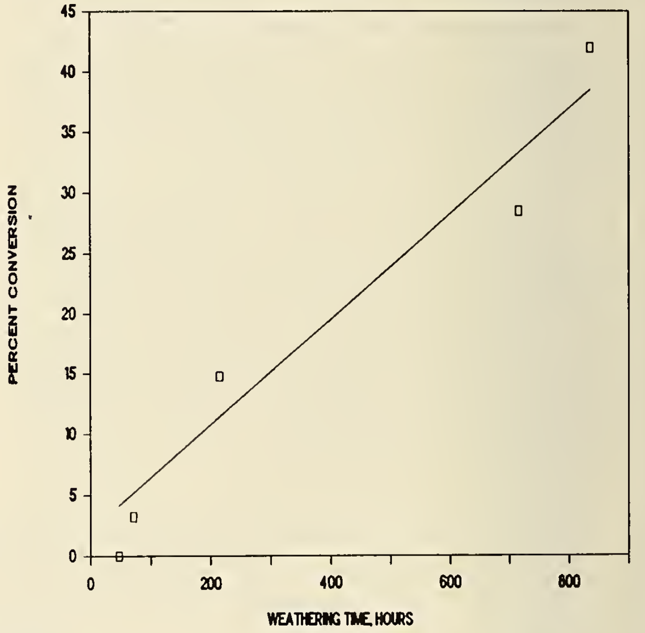

Figure 7. XPS monitored weathering of sedimentary/ hydrothermal pyrite (anthracite pyrite) at 21 pct. oxygen and 88 pct. relative humidity. Solid line denotes the least squares regression line used for rate calculations.

RESULTS AND DISCUSSION

XPS Tests

Plots of percent conversion of pyritic sulfur to sulfate sulfur versus weathering time (figs. 4-7) exhibited an initial linear region representing oxidation of about 40 to 90 percent of the available pyritic sulfur. Abiotic oxidation rates for each iron disulfide (table 2) were calculated from the slope of the least squares line fitted to the data in the initial linear region (solid line, figs. 4-7). Similar plots were obtained for tests at 5 pct and 10 pct oxygen.

The rates in table 2 reflect abiotic surface oxidation as measured by XPS. Because only pyritic sulfur and sulfate sulfur on the surface are detected, this technique can be used to compare the oxidation rates of iron disulfides with significantly different surface areas. Oxidation rates are simply the change in the sulfate sulfur:pyritic sulfur ratio with respect to time.

In samples with high surface area, more pyritic sulfur is detected by XPS, because more pyrite is exposed at the surface. Therefore, the technique compensates for differences in surface area and permits the oxidation of each iron disulfide to be monitored under near-ideal conditions. It is evident from the oxidation rates in table 2 that sedimentary pyrite is significantly more reactive than pyrite of high temperature (hydrothermal) origin irrespective of surface area. Sedimentary/hydrothermal pyrite, which originally formed at low temperatures (< 50°C) and was later metamorphosed, displayed a reactivity similar to hydrothermal pyrite. Even the specimen containing roughly equal parts hydrothermal pyrite and hydrothermal marcasite exhibited a reactivity that was closer to hydrothermal pyrite than to sedimentary pyrite.

The dependence of the abiotic oxidation of iron disulfides (initial rates) on oxygen content is shown in figure 8. Oxygen dependency ranges from no apparent dependence (0th order) in the case of hydrothermal pyrite to a significant dependence in the case of sedimentary pyrite. Both pyrite/marcasite and sedimentary/hydrothermal pyrite exhibited a similar but slight oxygen dependency. The number of oxygen partial pressures tested in this study is insufficient for formulating rate equations or determining reaction order. However, the difference in oxygen dependence between pyrites of pure sedimentary origin and pyrites of predominantly hydrothermal origin appears to be significant.

Sedimentary pyrite and pyrite/marcasite specimens reached an asymptotic level within the 800-hour experiments (70 pct. conversion, fig. 4 and 45 pct. conversion, fig. 5) where no further oxidation took place. The presence of an asymptote indicates that the mineral surface has become passivated. Possible explanations for this apparent passivation include the following:

1. The exhaustion of pyrite on the surface (applicable if XPS is detecting pyrite below the depth of weathering);
2. The exhaustion of a more reactive pyrite form (remaining pyrite oxidizes at a slow rate that is undetectable within the time frame of these tests);
3. In the case of sedimentary pyrite, organic sulfur in the form of thiophenes, thiols and organic sulfides would appear at the same binding energy as pyrite but would be unreactive;
4. A metal-deficient sulfide layer forms that cannot be distinguished from pyritic sulfur, but is unreactive and passivates pyrite surfaces.

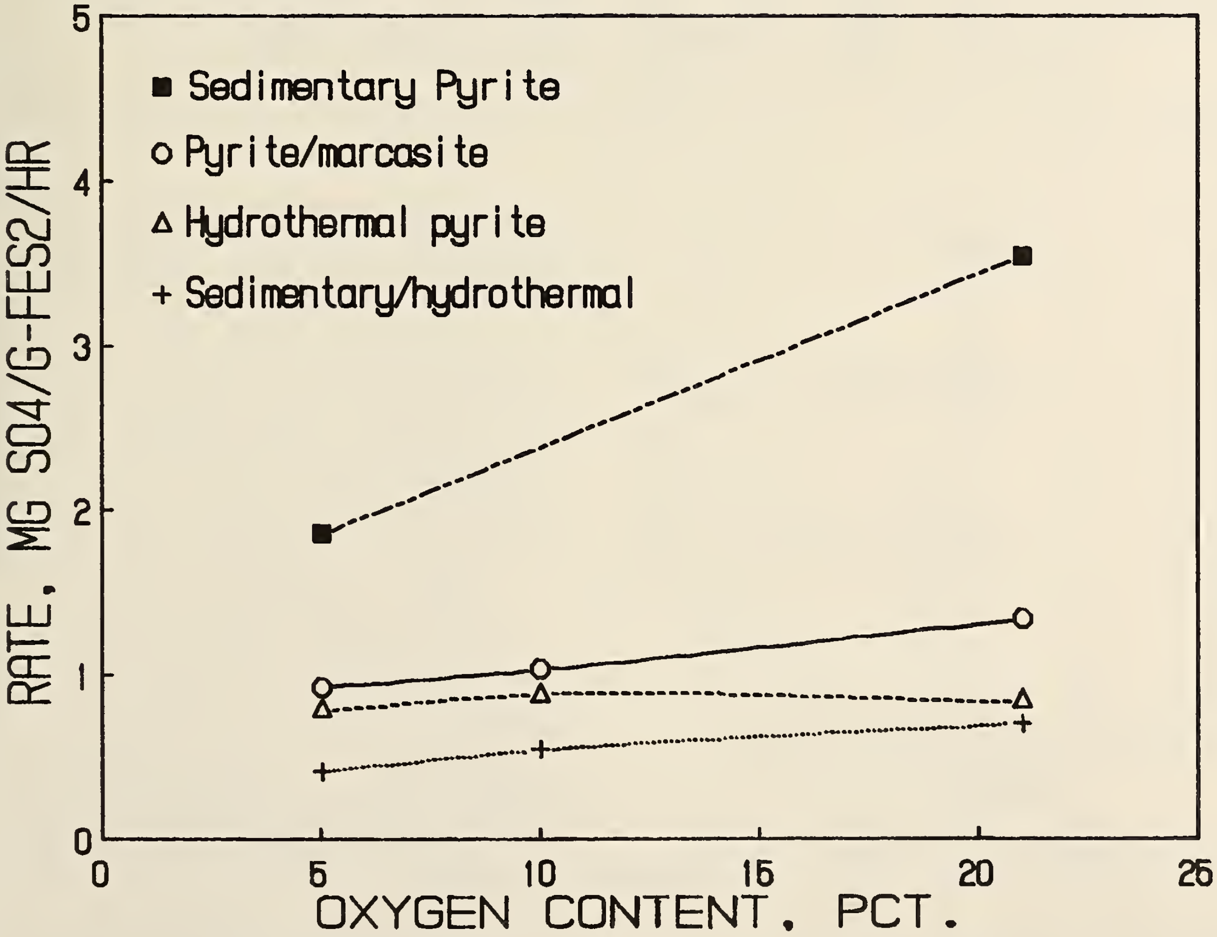

Figure 8. The dependence of oxidation rate on oxygen content.

Explanation 1 probably is not valid because we have observed in depth profiles (XPS analysis with argon ion sputtering), weathering 10-20 nm below the surface of sedimentary pyrite which is at least four times the analysis depth for XPS. Explanation 2 cannot be proved or disproved with current information. Explanation 3 may explain the presence of asymptotes in sedimentary pyrite plots, but not in hydrothermal pyrite/marcasite plots where no organic sulfur is present. Passivation due to the formation of a metal-deficient sulfide layer or the accumulation of oxidation products on the surface may best explain the asymptotes. Buckley and Woods (1986) found that upon weathering, a metal-deficient sulfide layer formed on pyrite which effectively passivated oxidation even in the presence of acetic acid. The S(2p) binding energy for this metal-deficient sulfide was 1- to 1.3-eV higher than that of pyrite and 0.3 eV lower than bulk elemental sulfur. In the work by Buckley and Woods, the metal-deficient sulfide only formed a small shoulder on the pyritic S(2p) peak (7 pct of the total S(2p) intensity). The resolution and the signal-to-noise ratio of the XPS instrument used in the present study were inadequate for the detection of metal-deficient sulfide layers.

EGA Tests

Plots of SO_2 partial pressure versus sample temperature are shown in figure 9. The mean temperature of the major peak for each iron disulfide increased in the following order: pyrite/marcasite (420°C), sedimentary pyrite (428°C), sedimentary/hydrothermal pyrite (470°C), and hydrothermal pyrite (499°C). When surface oxidation rate (21 pct oxygen, 88 pct relative humidity) measured by XPS is plotted versus the mean temperature of the major SO_2 evolution peak (fig. 10), two linear trends are observed. One trend, represented by five sedimentary pyrites, occurs at temperatures below 460°C with a slope of -0.103 mg SO_4 g^{-1} FeS_2 $hr^{-1}/°C$ ($r^2 = 0.9914$). The second trend is represented by three pyrites of predominantly hydrothermal origin and exhibits a slope of -0.007 mg SO_4 g^{-1} FeS_2 $hr^{-1}/°C$ ($r^2 = 0.8293$). A line connecting the two marcasite-containing samples parallels the slope of the sedimentary pyrite regression line, although it occurs at 30oC lower temperature. Based on the limited data available, sedimentary and hydrothermal pyrite appear to represent discrete populations that overlap at a SO_2 evolution temperature of 460°C. The linearity of the plot indicates that sedimentary pyrite specimens which are more susceptible to the high temperature, anhydrous oxidation in EGA, are also more susceptible to the hydrous oxidation in XPS tests that simulate the mine environment. However, the weathering rates for hydrothermal pyrite are low, irrespective of the major SO_2 evolution temperature displayed by the specimen.

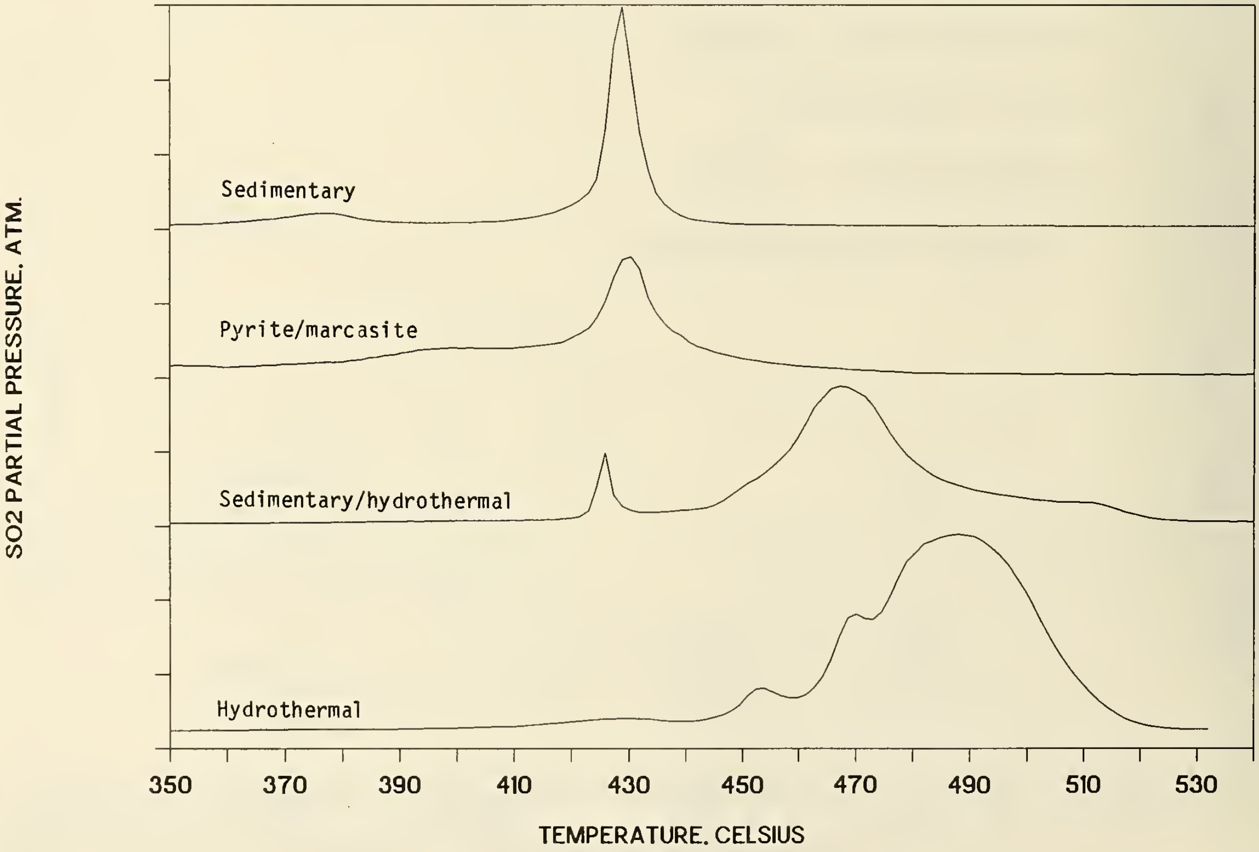

Figure 9. SO_2 thermograms of sedimentary pyrite, hydrothermal pyrite/marcasite, hydrothermal pyrite, and sedimentary/hydrdothermal pyrite.

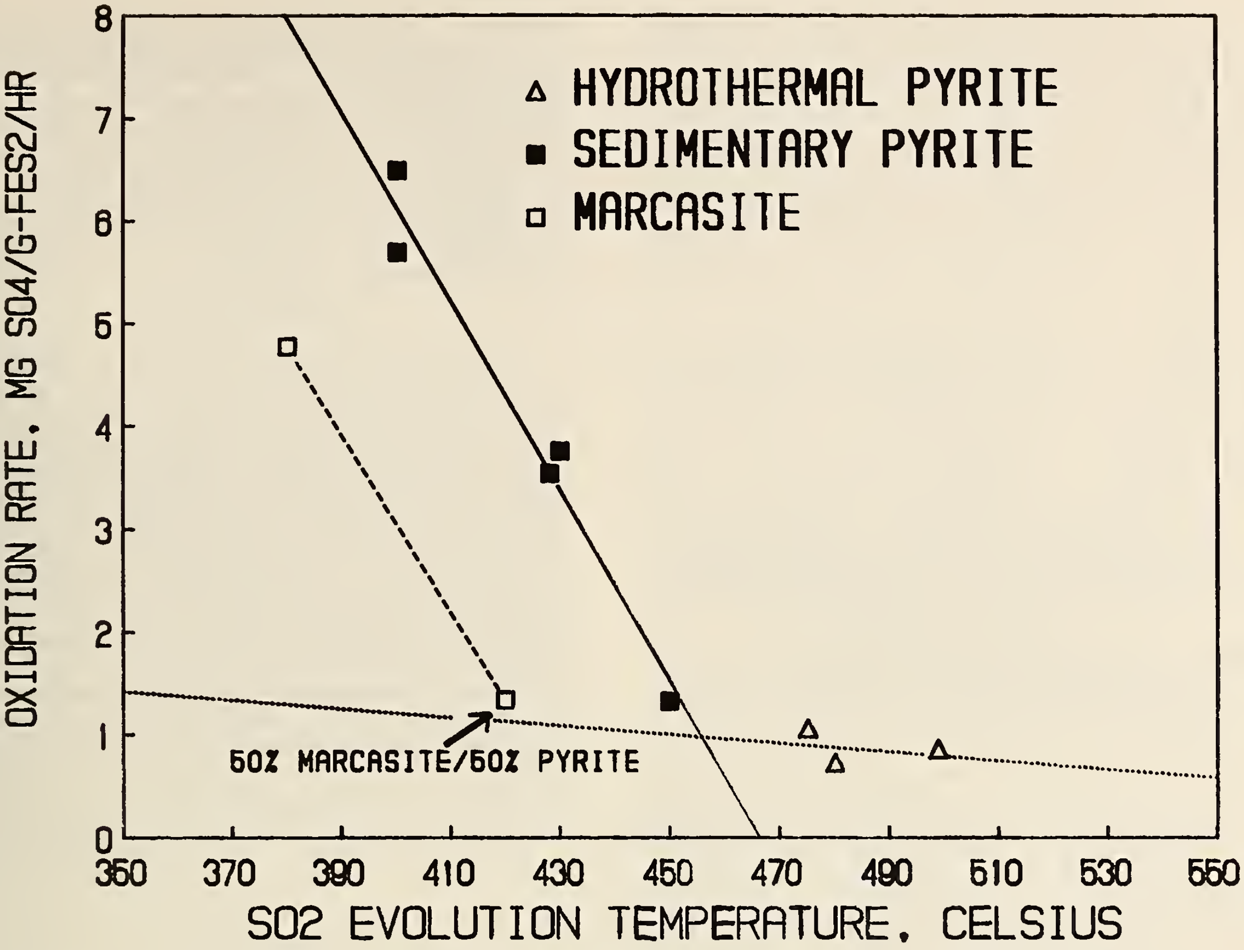

Figure 10. Plot of SO_2 evolution temperature from evolved gas analysis versus XPS monitored weathering rates.

The relationship between SO_2 evolution temperature and surface oxidation for sedimentary pyrites may permit EGA to be used as a quick method for determining surface oxidation rate. The sum of SO_2 peak areas was plotted versus mean evolution temperature for 16 coal samples from the Waynesburg, Upper Freeport, and Lower Kittanning coalbeds (fig. 11) and for 55 overburden samples from Pennsylvania, West Virginia, Maryland, Kentucky, and Illinois (fig. 12). The sum of the SO_2 peak areas is proportional to the total amount of pyrite with mean evolution temperatures within the 10°C interval. In both coal and overburden samples, most of the SO_2 is evolved from pyrite in the 420°C and 430°C intervals, which suggests that the abiotic surface oxidation rate is between 2.5- and 4.5 mg SO_4^{-2} g^{-1} FeS_2 hr^{-1}. Sulfur dioxide evolved at temperatures above 460°C is indicative of organic sulfur present in coal and other carbonaceous material (hydrothermal pyrite would also evolve SO_2 in this range if present). When the overburden samples (fig. 12) are compared with the coal samples (fig. 11), the distribution of the SO_2 peak areas appears to be 10°C higher in the case of the coal samples. This shift probably does not reflect a fundamental difference in pyrite reactivity, but rather a difference in sample preparation. The coal samples were crushed many months prior to EGA analysis, whereas the overburden samples were prepared and run within minutes. We have observed that with time and exposure to air, the SO_2 evolution temperature

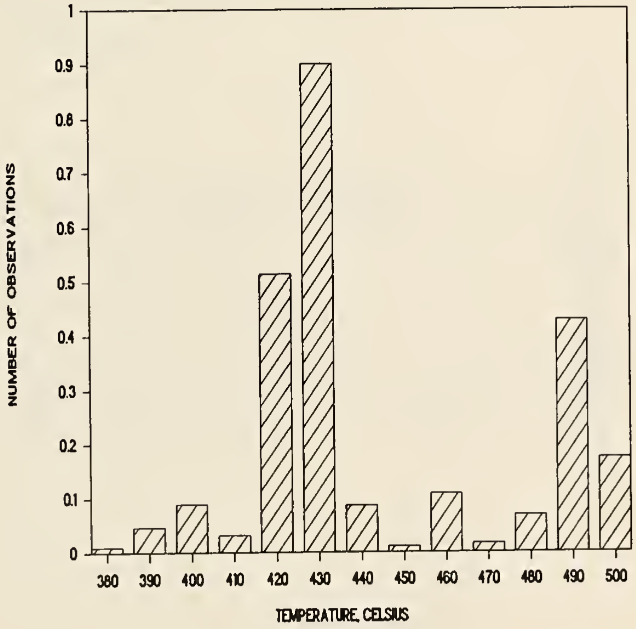

Figure 11. Distribution of SO_2 evolution temperatures for pyrite (<460°C) and organic sulfur (>460°C) in 25 coal samples.

increases. Another feature of these distributions is the small peak in the range of 380°C to 400°C that corresponds to the low temperature peak in the SO_2 thermogram of sedimentary pyrite (figs. 9 and 13). Pure marcasite also evolves SO_2 in this range (fig. 13) and it is possible that the small peak commonly observed in the SO_2 thermograms of sedimentary samples may represent marcasite. A small peak at 450°C (fig. 12) probably indicates that a more stable, epigenetic form of sedimentary pyrite is sometimes present.

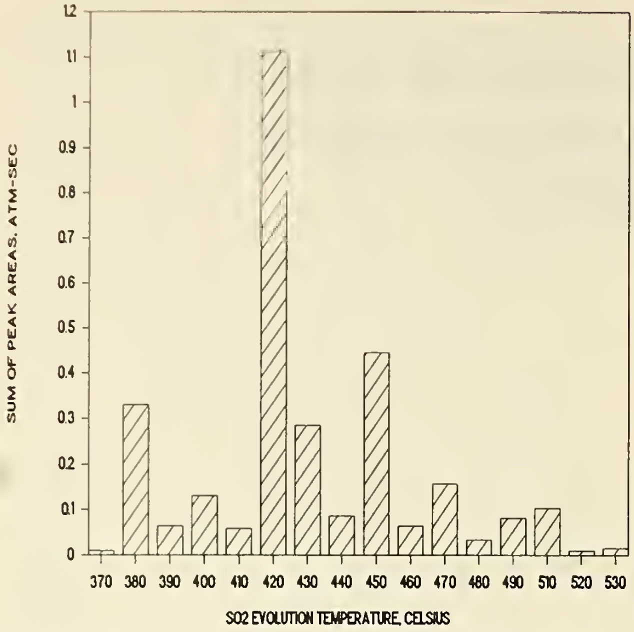

Figure 12. Distribution of SO_2 evolution temperatures for pyrite and organic sulfur in 55 over-burden samples.

Flotation Tests

XPS and EGA results indicate that sedimentary and hydrothermal iron disulfide surfaces exhibit significantly different reactivity. To help explain these differences, we used a simple froth flotation test to determine the charge developed on pyrite surfaces in aqueous solutions. This test consisted of placing a two-gram sample of -100 mesh pyrite in a 100-mL Pyrex glass flotation cell with a fritted bottom for gas bubbling. Each sample was conditioned in a solution containing 300 ppm anionic fluorosurfactant and 5 ppm sodium hydrosulfide, and then subjected to a three minute flotation. The froth and the residue were collected, dried, weighed, and the percentage flotation calculated. The flotation response of a sedimentary and a hydrothermal pyrite is given in Table 3.

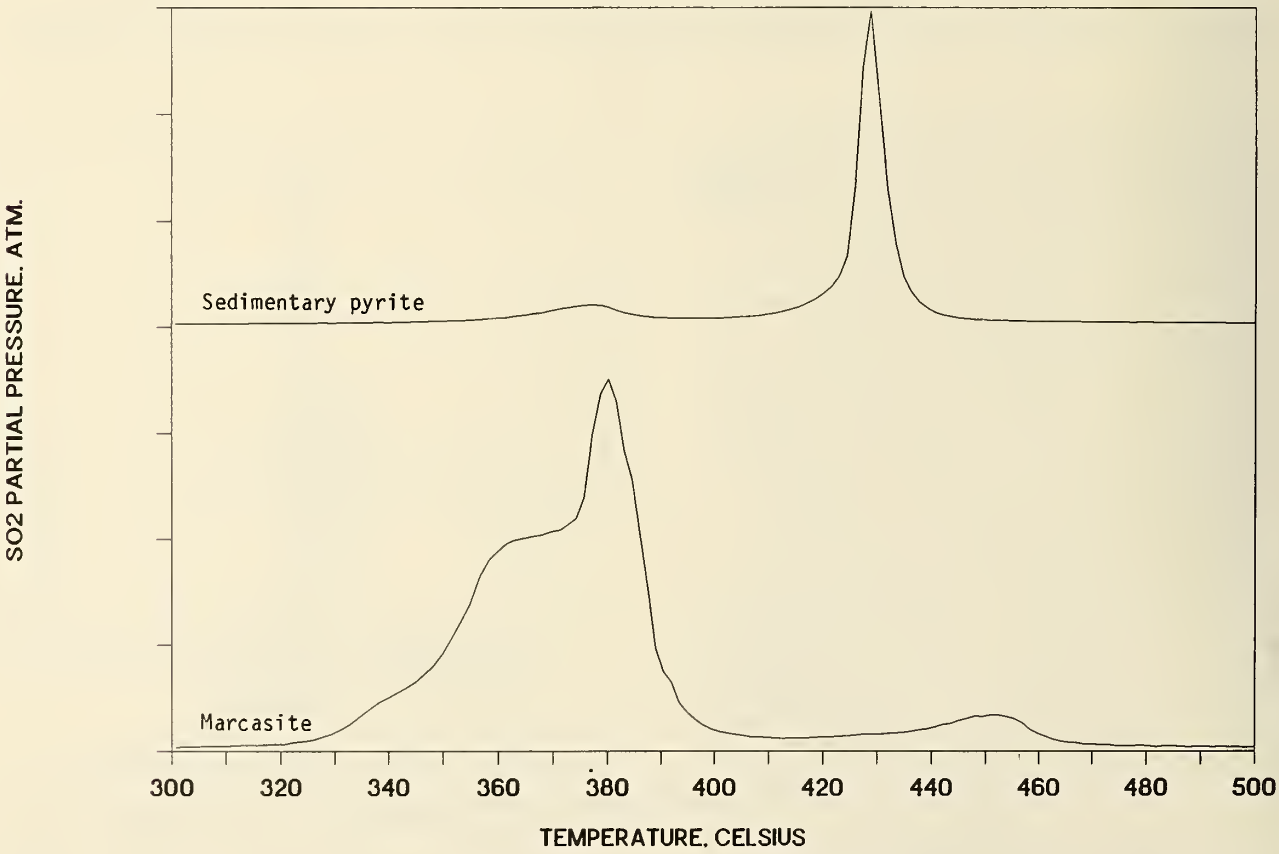

Figure 13. SO_2 thermograms of hydrothermal marcasite and sedimentary pyrite.

Table 3.--Flotation response of hydrothermal and sedimentary pyrites.

Sample	Wt. % Floated	Surface Charge
Hydrothermal pyrite	32	Positive
Sedimentary pyrite	<1	Negative

Hydrothermal pyrite and sedimentary pyrite differed substantially in flotation response. Hydrothermal pyrite was readily floatable (32 pct floated), indicating that its surface was positively charged and capable of electrostatically attracting the anionic collector. Adsorption of the collector rendered the surface hydrophobic and allowed the flotation of hydrothermal pyrite. Sedimentary pyrite was depressed, indicating that its surface was negatively charged and not able to interact with the anionic fluorosurfactant. The surface charge must be known in order to design coating agents that can be applied to pyritic material to limit oxidation. Because the charge on sedimentary pyrite surfaces is negative, a cationic species would provide the best coating. In the case of hydrothermal pyrite, an anionic species would be a better choice.

CONCLUSIONS

This study showed that pyrite of low-temperature origin (sedimentary pyrite) differs from pyrite of high-temperature origin (hydrothermal pyrite) in many basic properties:

1. The observed differences in oxidation rate between pyrites cannot be completely explained by differences in surface area;
2. The rate dependence of abiotic pyrite oxidation on oxygen content is considerably higher for sedimentary pyrite than for hydrothermal pyrite;
3. In evolved gas analysis, sedimentary pyrite evolves SO_2 at lower temperatures, indicating that it is more reactive than hydrothermal pyrite;
4. In plots of abiotic surface oxidation rate versus mean SO_2 evolution temperature, sedimentary pyrites and hydrothermal pyrites appear to form two discrete populations;
5. Surfaces of hydrothermal pyrite are positively charged (floats in flotation tests with anionic fluorsurfactant); surfaces of sedimentary pyrite are negatively charged (depressed in flotation tests).

Results of this study indicate that passivation of pyrite surfaces occurs rapidly once sufficient oxidation has taken place. This passivation is probably caused by the formation of a metal-deficient sulfide layer and the accumulation of oxidation products on pyrite surfaces. Passivation would probably not occur under field conditions where 1) there is sufficient moisture to dissolve and transport hygroscopic iron sulfates, and 2) there are bacteria that can oxidize metal-deficient sulfide layers.

A plot of surface oxidation rates measured by XPS versus SO_2 evolution temperatures from EGA can be described by two linear trends, one trend represented by five sedimentary pyrites, the second trend represented by three iron disulfides of predominantly hydrothermal origin. Based on these linear relationships, results from quick and simple EGA tests can now be used to calculate surface oxidation rates. For example, EGA results from 16 coal and 55 overburden samples indicate that the predominant surface oxidation rate for sedimentary pyrite is between 2.5- and 4.5 mg SO_4^{-2} g^{-1} FeS_2 hr^{-1}. These rates are abiotic rates based on available pyrite (pyrite at the surface) and cannot be directly applied to the field without considering surface area and bacterial catalysis. However, these results can be used to augment existing AMD predictive techniques by providing a qualitative ranking of iron disulfide reactivity. Their origin (sedimentary or hydrothermal) is critical to the type of behavior exhibited by iron disulfides. We know from previous work that sedimentary pyrites display a wide range of reactivities. The oxidation rates displayed by the three hydrothermal iron disulfides in the current study appear to be more consistent, perhaps reflecting a more highly ordered crystal structure. It is important to recognize that the fundamental properties of iron disulfides, particularly of sedimentary pyrite, can vary widely. Iron disulfides are similar in gross stoichiometry, but little else.

ACKNOWLEDGEMENTS

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INTERPRETATION OF ISOTOPIC COMPOSITIONS OF DISSOLVED SULFATES IN ACID MINE DRAINAGE

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Abstract.--Sulfates produced by oxidation of sulfide minerals in mines, mine-and-mill tailings, and waste-rock dumps are characterized by (1) $\delta^{34}S$ values similar to those of the original sulfide minerals, and (2) low or negative $\delta^{18}O$ values similar to those for sulfates in acidic spring waters. Experimental oxidation of pyrite in waters with a wide range of $\delta^{18}O$ values has shown that the $\delta^{18}O$ value of the product sulfate depends not only on the experimental conditions (aerobic or anaerobic; submerged or intermittently wet and dry; sterile or containing *Thiobacillus ferrooxidans*), which may determine the actual reaction pathways, but also on the $\delta^{18}O$ value of the water in which the oxidation takes place. The experimental results can be interpreted as evidence that 29 to 100% of the oxygen in the sulfate was derived from water molecules, whereas dissolved sulfates in field samples incorporated 35 to 90% water oxygen. So far it has not been possible to determine whether the water oxygen is incorporated into the sulfate during the actual oxidation process (as implied by proposed stoichiometric equations), or through oxygen-isotope exchange between the water and one or more intermediates (e.g. sulfite or thiosulfate). At room temperature, the exchange of oxygen isotopes between water and sulfate ions is too slow to effect the observed $\delta^{18}O$ values. The range in $\delta^{18}O$ values for sulfate produced by oxidation of sulfides tends to widen as $\delta^{18}O$ values for rain and snow become more negative at higher latitudes and at greater distances from the oceans. Some uncertainty still exists regarding the actual $\delta^{18}O$ value for dissolved oxygen in subsurface waters. A further complication is background sulfate from sources such as marine evaporites, which might be detected using sulfur isotope data. The above components must be characterized before proper interpretation of the oxygen-isotope composition of sulfate produced during sulfide weathering is possible. Only then could oxygen-isotope data be used to monitor the effects of measures designed to reduce (or accelerate) the oxidation process in mines, tailings deposits, and waste-rock dumps.

INTRODUCTION

It has been realized for some time that oxygen incorporated into sulfate during the oxidation of sulfide minerals is derived in part from molecular oxygen and in part from water molecules. The overall oxidation process is usually described by several stoichiometric equations. For example, Taylor et al. (1984b) cite the following:

$$2FeS_2+28Fe^{3+}+16H_2O \rightarrow 30Fe^{2+}+4SO_4^{2-}+32H^+ \quad [1]$$

$$28Fe^{2+} + 7O_2 + 28H^+ \rightarrow 28Fe^{3+} + 14H_2O \quad [2]$$

$$2FeS_2+7O_2+2H_2O \rightarrow 2Fe^{2+}+4SO_4^{2-}+4H^+ \quad [3]$$

If reaction [1] applies, all sulfate oxygen, Os, is derived from water molecules, Ow, whereas in reaction [3], 87.5% of the sulfate oxygen is derived from molecular oxygen, Om, and 12.5% from Ow. Reaction [2], which regenerates Fe^{3+} for reaction [1], produces H_2O from molecular oxygen. However, the amount of this H_2O is relatively minor and unlikely to affect the δ^{18}Ow and δ^{18}Os values.

It must be emphasized that the above equations, while convenient, may not describe the actual reaction mechanisms. For example, there is still considerable debate as to whether water dissociates and plays an oxidizing role, or whether exchange of oxygen isotopes between the water and intermediate sulfur species fully accounts for the presence of water oxygen in the product sulfate. According to Rimstidt et al. (1986), the process converting sulfide sulfur to sulfate may consist of as many as eight reaction steps, some of which occur at the mineral/solution interface, whereas others occur in the dissolved phase. Intermediate sulfur species may comprise polysulfides, elemental sulfur, polysulfonic acids, sulfite, and thiosulfate. Postulated pathways of sulfur oxidation by Thiobacilli invoke these intermediates (cf. review by Ralph 1979). There is, however, the question whether their concentrations and/or lifetimes, during natural oxidation of metal sulfides, are sufficiently large for exchange reactions to alter the oxygen isotope composition of the final sulfate product.

This paper examines published and new data for oxidation experiments and field samples, to determine how effectively oxygen-isotope data for dissolved sulfate in "acid mine drainage" can elucidate the conditions prevailing during the oxidation of metal sulfides. Isotopic data from laboratory experiments are available for oxidation of Na_2S and H_2S (Lloyd 1967, 1968); for oxidation of elemental sulfur (Mizutani and Rafter 1969); and for oxidation of pyrite (Schwarcz and Cortecci 1974; Taylor et al. 1984a; and current studies). Isotopic data for field samples have been published by Shakur (1979), Smejkal (1979), Taylor et al. (1984b), and van Everdingen et al. (1985); additional field samples have recently been analyzed by the authors.

METHODS

At the tailings deposit of an abandoned zinc mine in northern Ontario, water samples were collected from 2-inch (5-cm) ID piezometers, using a small-diameter bailer. The samples were stored in 1-L polyethylene and 125-ml glass bottles. The samples were used for the determination of δ^{34}S and δ^{18}Os values for dissolved sulfate, and δ^{18}Ow values for the water, respectively. At the same site, samples of tailings were collected from drillholes and testpits, and stored in plastic bags. Additional water samples were collected from mine drainage at two abandoned coal mines near Coleman (Alberta); from a tailings pond at a gold mine near Contwoyto Lake (N.W.T.); and from acidic creeks draining pyritic exposures near McBride (British Columbia), and near the Nanisivik lead/zinc mine on Baffin Island (N.W.T.).

In our oxidation experiments we used waters with four different δ^{18}Ow values, ranging from -33.5 to +34.0°/oo. For each type of water, two 125-mL vacuum flasks were prepared, each with 100 mL of water and 100 mg of pyrite that had been finely ground in dry air. The tops of the flasks were sealed with parafilm, while the side arms were left open to the atmosphere. After 31 days, the water was removed from one set of four flasks and analyzed to determine δ^{18}Os; after 547 days, 60 mL of water was removed from the second set of flasks and analyzed to determine both δ^{18}Os and δ^{18}Ow.

Sulfur and oxygen isotope analyses followed procedures described by Thode et al. (1961), van Everdingen et al. (1982), and Ueda and Krouse (1986).

In the following sections, oxygen and sulfur isotope data are reported as per mil (°/oo) δ^{18}O and δ^{34}S values, defined as:

$$\delta^{18}O = \left[\frac{[^{18}O/^{16}O]_{sample}}{[^{18}O/^{16}O]_{standard}} - 1\right] \times 10^3$$

$$\delta^{34}S = \left[\frac{[^{34}S/^{32}S]_{sample}}{[^{34}S/^{32}S]_{standard}} - 1\right] \times 10^3$$

The usual standards for δ^{34}S and δ^{18}O are troilite from the Cañon Diablo meteorite (CDT), and water approximating the mean isotopic composition of the ocean (SMOW).

Table 1.--Isotope data from oxidation experiments

SOURCE	DURATION (days)	$\delta^{18}Os$ °/oo SMOW	$\delta^{18}Ow$ °/oo SMOW	Δ °/oo
Current study - PYRITE (submerged/aerobic)	31	-5.9	-33.5	+27.6
	31	+0.7	-19.5	+20.2
	31	+16.0	+17.0	-1.0
	31	+22.6	+34.0	-11.4
	547	-14.2	-26.2 *	+12.0
	547	-5.7	-13.1 *	+7.4
	547	+15.6	+22.3 *	-6.8
	547	+29.5	+40.5 *	-11.0
Taylor et al., 1984a - PYRITE				
(submerged/anaer./sterile/+Fe^{3+})	30	-6.9	-10.9	+4.0
(submerged/aerobic/sterile/+Fe^{3+})	26	-6.0	-10.9	+4.9
(submerged/aerobic/sterile)	27	-4.8	-10.9	+6.1
(submerged/aerobic/+T.ferro.)	27	+1.8	-10.9	+12.7
(submerged/aerobic/+T.ferro.)	27	+0.5	-10.4	+10.9
(wet/dry, sterile)	29	+1.3	-10.9	+12.2
(wet/dry, sterile)	29	-0.9	-10.4	+9.5
(wet/dry, + T.ferro.)	29	+6.6	-10.9	+17.5
(wet/dry, + T.ferro.)	29	+7.7	-10.4	+18.1
Mizutani & Rafter, 1969 - SULFUR				
(in aerated water with soil)	14	-7.6	-7.0	-0.6
	17	-7.0	-7.0	0.0
	15	-1.3	-0.8	-0.5
	18	-0.4	-0.8	+0.4
	21	+2.0	-0.8	+2.8
Schwarcz & Cortecci, 1974 - PYRITE				
(in aerated water)	14	+3.5	-8.0	+11.5
	14	+71.0	+127.0	-56.0
Lloyd, 1967 - H_2S				
(through aerated water)	-	+2.0	-4.7	+6.7
	-	+18.0	+20.0	-2.0
	-	+29.3	+34.0	-4.7

* - Values at end of experiment reflect evaporation effects

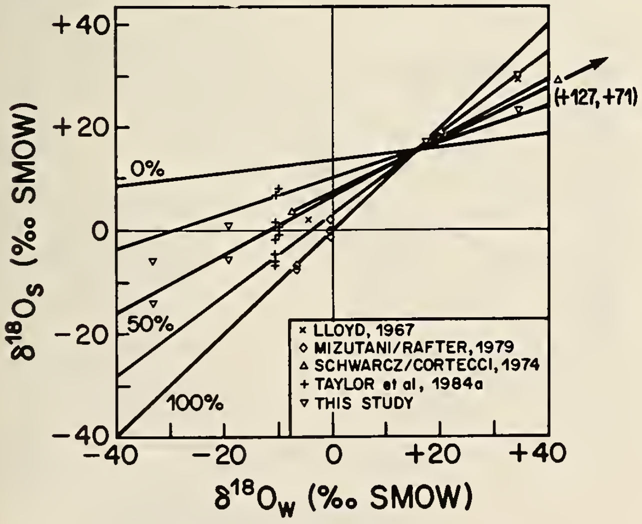

Figure 1.-- $\delta^{18}Os$ values of SO_4^{2-} versus $\delta^{18}Ow$ values of H_2O for oxidation experiments.

DATA FROM LABORATORY EXPERIMENTS

Isotopic data from oxidation experiments are listed in table 1 and illustrated by figure 1.

Previous Work

Lloyd (1967, 1968) concluded that the ratio of water oxygen to molecular oxygen used in the oxidation of Na_2S, at 25°C in water under an oxygen atmosphere, was 1:2. He suggested that the initial reaction (not balanced) was

$$S^{2-} + H_2O + O_2 \rightarrow SO_3^{2-} \qquad [4]$$

The isotope fractionation [εm] for the incorporation of molecular oxygen was deduced to be -8.7°/oo. Lloyd also found that the subsequent reaction

$$SO_3^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4^{2-} \qquad [5]$$

was comparatively slow, and that sulfite underwent oxygen-isotope exchange with the water (80% in one week at room temperature), as much as 10^5 times faster than the exchange between sulfate and water. The final $\delta^{18}Os$ for the sulfate would thus depend on the competing rates of (1) exchange of oxygen isotopes between sulfite and water, and (2) oxidation of sulfite to sulfate. It should be noted here that buildup and retention of SO_4^{2-} are pH dependent.

Oxidation of H_2S in aerated waters with three different $\delta^{18}Ow$ values resulted in 64 to 76 percent of the sulfate oxygen being derived from Ow (Lloyd 1967). The isotope fractionation [εw] for incorporation of water oxygen into SO_4^{2-} was found to be zero. The Δ values ($\delta^{18}Os$ minus $\delta^{18}Ow$) for individual samples ranged from -4.7 to +6.7°/oo (table 1).

Bacterially mediated oxidation of elemental sulfur in an aerated soil/water slurry at 30°C produced sulfate with $\delta^{18}Os$ values almost identical to $\delta^{18}Ow$ (Mizutani and Rafter 1969). Sulfur isotope fractionations between sulfur and sulfate were less than 2.3°/oo; Δ values ranged from -0.6 to +2.8°/oo (table 1).

Oxidation of finely ground pyrite at 25°C in aerated slurries made with waters with two different $\delta^{18}Ow$ values revealed that $\delta^{18}Os$ increased about 0.6°/oo for each °/oo increase in $\delta^{18}Ow$ (Schwarcz and Cortecci 1974). The Δ values ranged from -56.0 to +11.5°/oo, and approximately half the sulfate oxygen was deduced to have been derived from the water (table 1).

A series of experiments was designed by Taylor et al. (1984b) to elucidate the pathways of pyrite oxidation. They used both aerobic and anaerobic sterile conditions, as well as aerobic conditions with Thiobacillus ferrooxidans. The pyrite was either submerged or subjected to the alternating wet and dry conditions often found in mine environments. For individual experiments, the Δ values ranged from +4°/oo (anaerobic, sterile), to +18°/oo (aerobic, with T.ferro.). The isotope fractionation (εm) for incorporation of molecular oxygen into sulfate was found to be -4.3°/oo for chemical (abiological) oxidation, and -11.4°/oo for bacterially-mediated oxidation (for an "average" value of -7.9°/oo).

This Study

In our experiments, the samples extracted after 31 days showed Δ values ranging from -11.4 to +27.6°/oo; for the samples extracted after 547 days, the Δ values ranged from -11.0 to +12.0°/oo; the Δ value was smallest (1°/oo) for the experiment using water with a $\delta^{18}Ow$ value of +17°/oo.

DATA FOR FIELD SAMPLES

Isotopic data for most of the field samples are listed in tables 2 and 3, and illustrated in figure 2.

The Δ values ranged from +3.4 to +11.1°/oo for samples from Bohemia (Smejkal 1979); from +2.6 to +15.2°/oo for samples from Colorado and California (Taylor et al. 1984b); from +10.2 to +23.0°/oo for samples from W. and N. Canada (van Everdingen et al. 1985); and from +4.0 to +22.0°/oo for the samples analyzed during our current study. The Δ values for samples from the Pine Point area (N.W.T.), analyzed by Shakur (1979), were all higher, ranging from +26.4 to +34.0°/oo.

DISCUSSION

Isotope Balance Calculations

To help determine the relative fractions of sulfate oxygen produced by the model reactions [1] and [3] during the various experiments, the isotopic composition of the oxygen incorporated in sulfate during sulfide oxidation can be expressed by the isotopic balance equation:

$$\delta^{18}Os = Y * (\delta^{18}Ow + \varepsilon w) + (1-Y) * \\ * (0.875 * (\delta^{18}Om + \varepsilon m) + \\ + 0.125 * (\delta^{18}Ow + \varepsilon w)) \qquad [6]$$

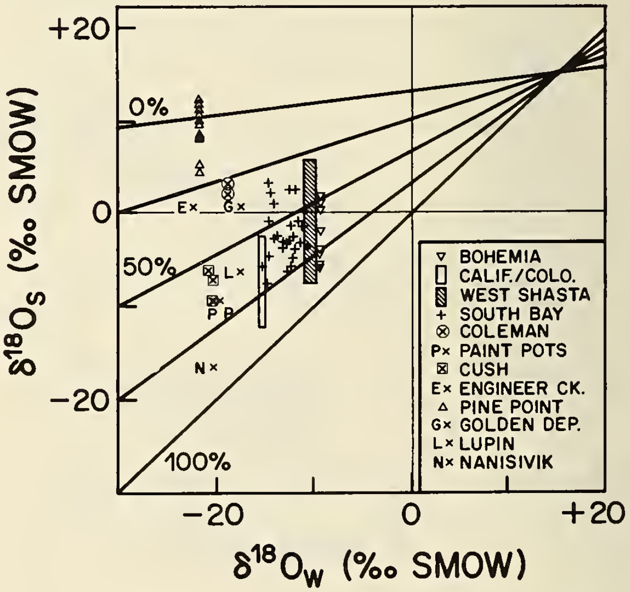

Figure 2.-- $\delta^{18}Os$ values of SO_4^{2-} versus $\delta^{18}Ow$ values of H_2O for field samples.

Table 2.-- Isotope data for field samples

	Sulfate		Water	
SOURCE	$\delta^{34}S$ ^{o}/oo CDT	$\delta^{18}O$ ^{o}/oo SMOW	$\delta^{18}O$ ^{o}/oo SMOW	Δ ^{o}/oo
A - ACIDIC SPRINGS				
PAINT POTS, B.C.				
Spring #12, 3-7-81	+10.8	-9.4	-20.5	+11.1
Spring #12, 28-4-84	+9.4	-9.5	-19.7	+10.2
GOLDEN DEPOSIT, N.W.T.				
Spring Water	-22.8	+0.5	-17.7	+18.2
ENGINEER CREEK, YUKON				
Acid Discharge	-23.2	+0.5	-22.5	+23.0
CUSH PROPERTY, B.C.				
Water 80158	+1.3	-6.2	-21.0	+14.8
Water 80159	+0.9	-9.4	-20.4	+11.0
Water 80160	+1.1	-7.2	-20.5	+13.3
NANISIVIK, N.W.T.				
Acid Creek #2	+15.3	-16.4	-20.4	+4.0
B - MINE WATERS				
W. and N. BOHEMIA (Smejkal (1979)				
Michael coal mine		+1.6	-9.5	+11.1
Antonin coal seam		+0.8	-9.5	+10.3
Josef coal seam		+0.1	-9.5	+9.6
Hromnice quarry, pyritic slates		-6.1	-9.5	+3.4
Berk quarry, pyritic slates		-2.1	-9.5	+7.4
Tisova sulfide mine		-4.1	-9.5	+5.4
Svornost sulfide mine		-4.7	-9.5	+4.8
Jachymov, Geier sulfide vein		-5.9	-9.5	+3.6
COLORADO/CALIFORNIA (Taylor et al. 1984a, Fig. 2)				
Mine waters Minima		-12.3	-15.7	+3.4
Maxima		-2.7	-15.1	+12.9
W. SHASTA, California (Taylor et al. 1984a, Fig. 2)				
Mine waters Minima		-7.6	-11.1	+2.6
Maxima		+5.7	-9.8	+15.2
COLEMAN, Alberta				
CC Mine Drainage	+19.6	+1.9	-19.1	+21.0
WCC Mine Drainage	+18.6	+3.0	-19.0	+22.0
LUPIN MINE, N.W.T.				
Tailings Pond	+3.2	-6.3	-17.6	+11.3
PINE POINT, N.W.T. (Shakur, 1979)				
Water from open pit	+14.4	+9.8	-22.0	+31.8
	+15.0	+8.6	(ave.)	+30.6
	+16.5	+9.8		+31.8
	+11.9	+5.2		+27.2
	+16.5	+12.0		+34.0
	+17.0	+11.0		+33.4
	+18.7	+11.0		+33.0
	+12.8	+8.2		+30.2
	+11.7	+4.4		+26.4
	+16.3	+11.4		+33.4
	+15.5	+8.8		+30.8
	+17.7	+10.4		+32.4
	+18.2	+12.0		+34.0
	+17.7	+11.0		+33.0

Table 3.-- Isotope data for South Bay mine tailings.

WATER SAMPLES

Piezometer #	Depth, m	Sulfate $\delta^{34}S$ °/oo CDT	Sulfate $\delta^{18}O$ °/oo SMOW	Water $\delta^{18}O$ °/oo SMOW	Δ °/oo
H - 5	1.3 - 2.2	+4.5	-0.9	-11.7	+10.8
H - 5	1.3 - 2.2	+4.6	-3.3	-11.5	+8.2
H - 6	1.4 - 2.3	-0.8	-3.4	-12.9	+9.6
H - 7	1.8 - 2.7	+0.2	-6.3	-12.8	+6.5
H - 8	1.2 - 2.1	-0.6	-5.7	-15.5	+9.8
H - 8	1.2 - 2.1	-0.1	-7.6	-14.9 *	+7.3
M - 4	4.4 - 5.1	+0.6	-1.5	-12.4	+10.9
M - 5	10.3 - 10.6	+0.1	+2.4	-12.1	+14.5
M - 5b	4.8 - 5.1	-0.9	-5.7	-12.5	+6.8
M - 7a	3.8 - 4.6	0.0	-3.9	-12.0	+8.1
M - 7b	9.8 - 10.1	+0.6	-3.8 *	-10.8 *	+7.0
M - 8	7.9 - 8.2	-0.1	-4.8	-12.3	+7.4
M - 9	5.5 - 5.8	-0.2	-4.7	-14.9	+10.1
M - 11	5.9 - 6.8	+0.9	-3.1	-12.7 *	+9.7
M - 18	7.0 - 7.9	+8.3	+0.8	-14.2	+15.1
M - 24a	7.3 - 8.1	-0.2	-1.0	-14.8	+13.8
M - 24b	4.4 - 5.2	0.0	-2.8 *	-14.2	+11.4
M - 2	16.9 - 17.2	+0.3	+3.2	-14.8	+18.0
M - 32	9.9 - 10.2	+0.1	-3.7	-13.3	+9.5
M - 40	5.4 - 6.2	+2.5	-1.4	-11.4	+9.9
M - 41	4.1 - 4.9	+0.6	+2.4 *	-12.7	+15.0
M - 43	8.9 - 9.2	-0.2	-2.6 *	-14.0	+11.4
M - 45	5.9 - 6.2	-0.1	-3.3	-13.4 *	+10.2
M - 4	10.4 - 11.0	-0.3	-2.6	-12.3	+9.6
M - 49	2.6 - 2.9	-0.6	+2.0	-14.7	+16.7

TAILINGS SAMPLES

Source	Depth, m	State of oxidation	Sulfide $\delta^{34}S$ °/oo CDT	Sulfate $\delta^{34}S$ °/oo CDT	Sulfate $\delta^{18}O$ °/oo SMOW
H - 2 T1	0.41 - 0.45	OX	+0.8	+1.4	-4.8
H - 2 T2	1.83 - 2.43	UNOX	+0.8	+0.4	+0.8
M - 4 T	1.52 - 2.13	UNOX	+1.1	+0.3	-0.9
M - 26 T	1.52 - 2.13	UNOX	+0.5	-4.8 *	+4.0
M - 27 T	1.52 - 2.13	UNOX	+1.2	+0.6	-2.6
M - 40 T	1.52 - 2.13	UNOX	+0.9	+0.6	-5.9
M - 43 T1	0.43 - 0.50	OX	+1.2	+1.8	+4.2
M - 43 T2	1.22 - 2.43	UNOX	+0.8	+0.7	+5.6
M - 46 T1	0.41 - 0.50	OX	+1.2	+1.3	-4.2
M - 46 T2	0.51 - 0.60	OX	+1.0	+1.0	-6.4
M - 46 T3	1.52 - 2.13	UNOX	+1.3	+0.7	-6.2
CONCENTRATE SAMPLE		OX	+0.4	-1.3	+0.1

* - Average of two determinations

in which Y is the fraction of sulfate ions produced by reaction [1]; εm and εw represent the shifts in δ^{18}Om and δ^{18}Ow during incorporation of Om and Ow into sulfate.

Using εm = -8.7°/oo and εw = 0.0°/oo (Lloyd 1967), and the δ^{18}Om = δ^{18}O of atmospheric O_2 = +23.8°/oo (Horibe et al. 1973), equation [6] can be rewritten as

$$\delta^{18}Os = \delta^{18}Ow * (0.875 * Y + 0.125) + \\ + (1-Y) * 13.21 \qquad [7]$$

Lines for 100, 75, 50, 25, and 0 percent contribution by reaction [1], calculated using equation [7], have been plotted in figures 1 and 2. These lines converge and intersect at the point representing δ^{18}Os = δ^{18}Ow ≈ +15°/oo. The convergence suggests that at low latitudes, where δ^{18}Ow values are closer to 0°/oo, it will be more difficult to distinguish contributions from individual reactions than at high latitudes, where δ^{18}Ow values may approach -30°/oo. It is noted that in the earlier analysis of van Everdingen and Krouse (1985), εw was chosen as +2.6°/oo, as suggested by data of Taylor et al. (1984a). However, with that εw value, some of our recent data would fall below the 100 percent reaction [1] line on a δ^{18}Os vs. δ^{18}Ow plot. Therefore, an εw value of zero seems more appropriate.

Equation [7] can be rewritten to allow calculation of Y from the δ^{18}Os and δ^{18}Ow values for individual samples:

$$Y = (\delta^{18}Os - 0.125 * \delta^{18}Ow - 13.21)/$$

$$/ (0.875 * \delta^{18}Ow - 13.21) \qquad [8]$$

Finally, the fraction (X) of sulfate oxygen derived from Ow can be calculated either from

$$X = 0.875 * Y + 0.125 \qquad [9]$$

or directly from the isotopic data for Os, Ow, and Om:

$$X = (\delta^{18}Os - (\delta^{18}Om + \varepsilon m)) /$$

$$/ (\delta^{18}Ow - (\delta^{18}Om + \varepsilon m)) \qquad [10]$$

The position of individual data points in relation to the percent-reaction-[1] lines in figures 1 and 2 indicates the proportions of the sulfate produced by reactions [1] and [3]. The spread of the experimental data (fig. 1) shows that between 19 and 100% of the sulfate can be produced by reaction [1]. This corresponds with 29 to 100% of the sulfate oxygen being derived from Ow (calculated by equation [9]). The distribution of the field data (fig. 2), with the exception of the Point Point set, indicates that 26 to 88% of the sulfate was produced by reaction [1], with 35 to 90% of the sulfate oxygen provided by Ow.

Complications in Field Situations

Sulfate in waters associated with sulfide mineralization may have been derived from several sources (fig. 3). In the case of carbonate-hosted metal-sulfide deposits, anhydrite (or gypsum) may have been dissolved earlier from associated marine evaporite strata. Under anaerobic conditions in the presence of a suitable carbon source, sulfate reduction may occur, enriching the remaining SO_4^{2-} in both ^{34}S and ^{18}O (cf. Krouse 1987). Under more aerobic conditions, sulfur in lower valence states can oxidize, incorporating oxygen atoms from dissolved O_2 and from H_2O.

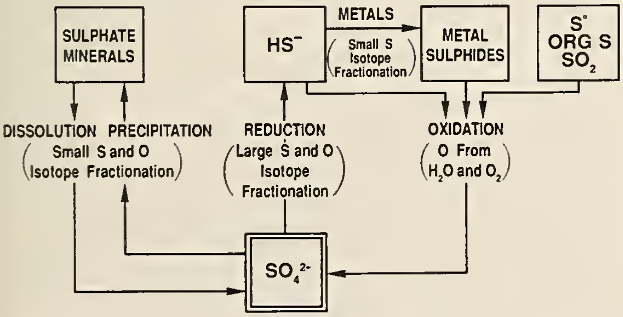

Figure 3.--Interactions between natural subsurface sulfate sources.

Interpreting isotopic data solely on the basis of metal-sulfide oxidation ignores the possibility that the water in which the oxidation process takes place may contain dissolved sulfate from non-sulfide sources. Where this is suspected, it is necessary to obtain information on both the concentration and the $\delta^{18}Os$ for the "original" sulfate.

The complexity of natural systems is illustrated by the data for water samples from a pumped open pit in the carbonate-hosted Pb/Zn deposit at Pine Point (Shakur 1979). The $\delta^{34}S$ and $\delta^{18}Os$ values varied by 6°/oo and 8°/oo, respectively (fig. 4), over a small area. The δ-values tended to increase with $[SO_4^{2-}]$ and $[Cl^-]$. The two known local sources of SO_4^{2-} are dissolution of anhydrite, and oxidation of metal sulfides, both with $\delta^{34}S$ values near +20°/oo (Sasaki and Krouse 1969).

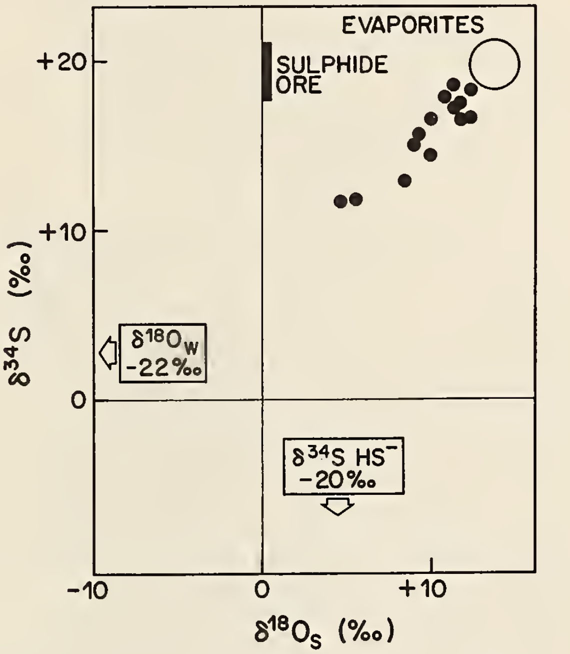

Figure 4.--$\delta^{34}S$ versus $\delta^{18}Os$ for SO_4^{2-} samples from an open pit near Pine Point, N.W.T. (after Shakur 1979). Ranges of $\delta^{34}S$ values for Pb-Zn ores, and of $\delta^{34}S$ and $\delta^{18}O$ values for evaporite sulfate are indicated.

A graphic tool for identifying sulfate sources is the plotting of δ-values versus the inverse of $[SO_4^{2-}]$ or $[Cl^-]$ concentrations. If a linear behaviour is invoked, the Y-intercept corresponds to the δ-value for one of the sources (cf. Krouse 1980). For the Pine Point $\delta^{18}Os$ data, figure 5 shows that the $\delta^{18}Os$ value at the intercept is 2 to 3 per mil higher than expected for the evaporite sulfate (Sasaki and Krouse 1969). Note that the line computed with the points for the two lowest sulfate concentrations excluded, gives an intercept close to the evaporite value.

It can also be argued that the $\delta^{18}Os$ values for many of these samples were somewhat elevated by bacterial sulfate reduction, because the Eh values of these waters average -250 mV (Shakur 1979). This would tend to give a lower Y-intercept, since higher $\delta^{18}O$ shifts

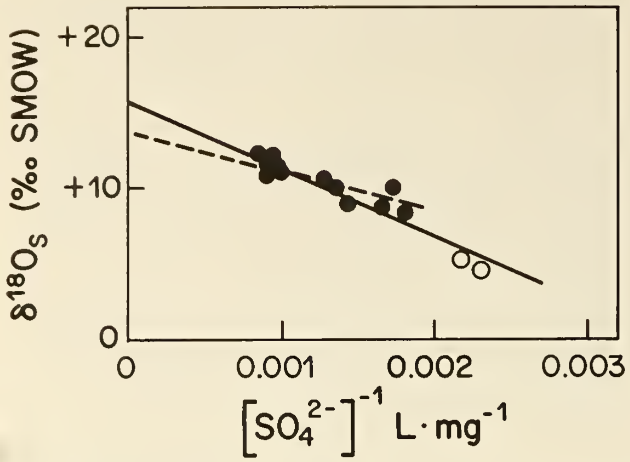

Figure 5--.δ^{18}Os versus the inverse of sulfate concentration, for water samples from an open pit near Pine Point, N.W.T. (after Shakur 1979). The dashed regression line represents the closed circles only (see text for discussion).

would be associated with lower sulfate concentration. The lower δ^{18}Os values in figure 5 imply that some sulfate was generated by oxidation of lower valence sulfur. The sulfide minerals cannot be the source for this, because their minimum δ^{34}S value is about +17°/oo, whereas figure 4 shows that lower δ^{34}S values were found for SO$_4^{2-}$. Note that the two samples with the lowest δ^{18}Os values and sulfate concentrations in figure 5 also have the lowest δ^{34}S values, and that they seem to fit a trend that differs from that suggested by the rest of the data in figure 4. Therefore, one may conclude that oxidation of another source of lower valence sulfur, with a lower δ^{34}S value, has produced some of the sulfate. Analysis of waters from boreholes some distance from the mining area revealed significant concentrations of δ^{34}S-depleted HS$^-$, generated by bacterial sulfate reduction (Weyer et al. 1979). Its re-oxidation would seem to be a good candidate for the third sulfate source. It can be readily appreciated that quantification of the sulfate contribution from the oxidation of sulfide ores in such a system would be impossible without detailed chemical and isotopic data.

Of our field data listed in tables 2 and 3, those for the Pine Point area are undoubtedly affected by the presence of marine sulfate, as discussed above. Those for the Golden Deposit and the Coleman mines are possibly affected; their δ^{18}Os values are relatively high, and evaporites are known to occur in their vicinity. No marine sulfates occur near the remaining sites; these include the South Bay and Lupin mines, located on the Canadian Shield, and the Nanisivik and Paint Pots discharges with the lowest δ^{18}Os values in table 2.

Other Uncertainties

Some uncertainty still exists regarding the δ^{18}Om value to be used in equations [6] and [10] for dissolved molecular oxygen participating in sulfide oxidation. In laboratory experiments, the δ^{18}Om value for atmospheric O$_2$ (+23.8°/oo, Horibe et al. 1973) has been assumed. However, the δ^{18}Om value of dissolved oxygen is usually not determined, although it may be drastically affected either by kinetic isotope effects during oxidation reactions, or by exchange processes. Determining δ^{18}Om values in natural waters presents a challenge because of difficulties during sampling. Even if a sample can be obtained without introducing atmospheric contamination, there is still the question as to whether the measured δ^{18}Om value represents that existing during sulfate formation. Nevertheless, attempts should be made to measure this parameter as it bears directly on the interpretation of δ^{18}Os versus δ^{18}Ow plots for field samples.

In addition it could be argued that the water associated with the sulfate at the time of sample collection may not properly reflect the δ^{18}Ow value of the water that provided the oxygen for incorporation into the sulfate. It should also be noted that water samples from a shallow tailings deposit can be expected to show a relatively wide range of, and some seasonal variation in, δ^{18}Ow values (reflecting δ^{18}Ow variations in infiltrating rain and snowmelt), as compared to water from natural acidic discharge or mine drainage, in which subsurface mixing would be more complete.

Holser et al. (1979, p. 14) asked: "Will field studies of pyrite oxidation, including isotope measurements on the oxygen of the air and water, ratify the ratio of 1:2 of those participants in Lloyd's experiments?". The authors believe that the data presented here have provided an answer to that question, even while raising several other questions. Careful selection and detailed analysis of samples from a variety of field situations should resolve some of the uncertainties outlined above. The paucity of experimental data on the proportions of Os derived from Om and Ow during oxidation of different sulfide minerals, elemental sulfur, and different organic sulfur species is being addressed by the authors in collaboration with a number of colleagues. Future oxidation experiments should be aimed at trapping (in sufficient quantity for isotopic analysis), one or more of the intermediate sulfur species that may be formed during the oxidation process, before they have a chance either to oxidize further or to exchange oxygen with the surrounding water.

CONCLUSIONS

Simplified stoichiometric equations describing pyrite oxidation, in combination with experimentally determined isotope parameters, define a field on a δ^{18}Os versus δ^{18}Ow diagram. Data from laboratory experiments, as well as data for samples from aerobic environments not affected by marine sulfate, were found to plot within this field. This suggests that the equations may present a reasonable, simplified description of the overall oxidation process. Calculations based on these equations indicate that the fraction of sulfate oxygen Os derived from water molecules ranges from about 29 to 100% for the experiments, and from 35 to 90% for the field samples.

The available experimental results also suggest that some of the water oxygen may be incorporated in the sulfate as a result of exchange of oxygen isotopes between the water and one or more intermediate sulfur species. The possibility that oxygen derived from H_2O molecules can act as an oxidant in purely chemical conversions, tends to be discounted.

The δ^{18} Os values for samples from some of the field sites reflect the presence of sulfate of marine-evaporite origin. In addition, the data for the Pine Point samples indicate the presence of sulfate derived from oxidation of HS^- which was generated earlier by bacterial sulfate reduction. Clearly, such background SO_4^{2-} must be characterized before δ^{18}Os and δ^{18}Ow data can be used to monitor sulfide oxidation in mining environments.

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GEOCHEMISTRY OF ABANDONED LIGNITE MINE SPOIL IN TEXAS

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Abstract--Geochemical investigations of lignite mine spoils ranging in age from 10 years to over 35 years were performed at an abandoned mined land reclamation project near Rockdale, Milam County, TX. A primary objective was to determine the degree to which oxidation of pyritic material had progressed for the design of an appropriate reclamation plan. For this purpose, eight continuous cores were recovered from the project area. The results indicated that within 10 years, consistent trends had already developed in the spoil among the principal sulfur forms (organic sulfur, pyritic sulfur, and sulfate sulfur). Three principal trends were identified: a gradual decrease in the proportion of sulfate sulfur to pyritic sulfur from the spoil surface downwards; a change, marked by a transition zone which varied in location and definition according to the age of the spoil, from low pH values (less than pH 4.0) in near-surface spoil to higher pH values (greater than pH 5.0) at greater depths; a trend with age of spoil to the correlation between the pH transition zone and the proportion of sulfate sulfur. These trends, associated with the processes of oxidation and leaching, are depicted on triangular graphs which are also used to show the reconstructed evolution of the spoil sulfur forms at ten-year intervals. The results of the geochemical investigations have been incorporated in the reclamation plan which is designed to minimize the exposure, through regrading, of spoil still containing pyritic sulfur forms.

Additional Key Words: pyritic sulfur, acid-forming material, sulfur forms, vadose zone.

INTRODUCTION

The work described in this paper was part of a reclamation program prepared for the Railroad Commission of Texas for the mitigation of an abandoned mined land reclamation project, near Rockdale, TX. Significant mining of lignite with draglines began in this area in the early 1950's and terminated in the project area with the passing of the Surface Mining and Reclamation Act of 1977. The spoils in the area, therefore, range in age from over 35 years old to 10 years old.

One of the principal objectives of the project was to determine the degree to which oxidation of pyritic sulfur had progressed and thus to assess the extent of acid and acid-forming materials for the reclamation plan (Railroad Commission of Texas, 1987). This paper deals specifically with the relationships discovered among the sulfur forms and pH values in the spoil.

MATERIALS AND METHODS

The data presented in this paper are based on eight continuous cores collected in the project area spoil. The project area covers approximately 1,200 acres and is located near Rockdale in Milam County, TX. The spoils are derived from the lignite-bearing formations of the Eocene Wilcox Group.

Core sites were selected on the basis of geographic and geologic settings to be representative of the project area. Since there was no detailed information available on the premining overburden geology and geochemistry, the principal criteria in site selection were to represent the 4 project subareas with an appropriate spatial distribution, to select sites showing a regular dragline spoiling pattern, and to distribute the sites in both geologically up-dip and geologically down-dip locations.

At each site, a small bulldozer was first used to prepare a drilling platform on the spoil ridge. This resulted in a small loss of sample corresponding, on average, to the top 5 ft. of the spoil. All sample depths have been adjusted accordingly and are reported in relation to the original spoil surface. A truck-mounted, hollow-stem auger (3-inch internal diameter) with a wire-line attachment for a Shelby tube was then used to collect the spoil samples. The hollow-stem system eliminated the potential contamination from drilling fluids or material falling in from the sides of the borehole. Cores were recovered to a depth approximately 4 ft. below the expected final topography after regrading. The core lengths varied in depth from 19.0 to 49.7 ft. A total of 264.4 ft. of spoil core was collected.

Each core was inspected and described in the field by an experienced geologist, sealed in plastic bags, labelled and boxed. Selection of sampling intervals was performed by an experienced soil scientist on the basis of the lithologic description and further examination of the core. A total of 51 sampling intervals were selected with a range of sample interval length from 0.6 ft. to 13.8 ft. and an average of 5.2 ft.

The laboratory methods used for the analysis of the spoil samples were those recommended by the Railroad Commission of Texas (1985). Sulfur forms (organic sulfur, pyritic sulfur, and sulfate sulfur) were determined according to EPA method 3.2.6 (EPA 1978), which separates the sulfur forms by extractant: HCl-extractable sulfur (mostly sulfates), HNO_3-extractable sulfur (mostly pyritic sulfur), and non-extractable sulfur (mostly organic sulfur). The extracted fractions were then submitted for sulfur analysis using an induction furnace and automatic sulfur titrator. The spoil reaction (pH) was determined on a 1:1 soil:water extract according to Black's method 60-3.4 (Black 1965).

A quality check was performed on the laboratory results testing for internal consistency with other geochemical parameters (not described in this paper).

RESULTS AND DISCUSSION

An examination of the proportions of sulfur forms (organic sulfur, pyritic sulfur, and sulfate sulfur) in the spoil showed that there were some general trends in the geochemistry with depth (Table 1). The principal trend is illustrated in spoil core GC-1 (fig. 1). Near the surface of the spoil [sample 1 (7.0-11.0 ft)] the pyritic sulfur content is zero and the only sulfur forms present are organic sulfur and sulfate sulfur. At successively greater depths [sample 2 (11.0-12.6 ft); sample 3 (12.6-16.4 ft); and sample 4 (16.4-24.0 ft)] the proportion of sulfate sulfur decreases while the proportion of pyritic sulfur increases. At still greater depths [sample 5 (24.0-31.2 ft)] the pyritic sulfur proportions are high and the sulfate sulfur proportions are low (generally below 15% of the

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement, April 17-22, 1988, Pittsburgh, P.A.)

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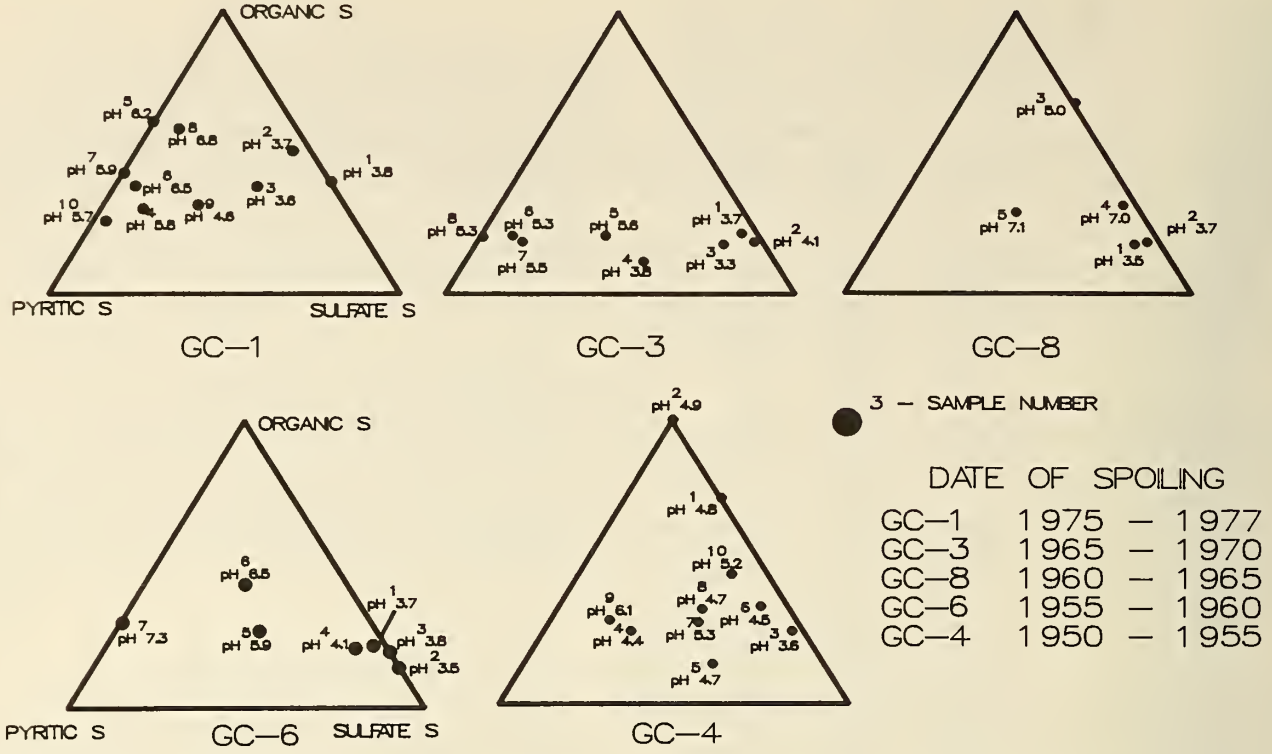
TABLE 1 - Contents of Sulfur Forms in Spoil Cores From Abandoned Lignite in Mine Spoil.

			Laboratory Analyses of Sulfur Content				Relative Content Among Sulfur Forms				
Spoil Core	Sample Number	Depths (feet)	Total Sulfur	Sulfate Sulfur	Pyritic Sulfur	Organic Sulfur	Total Sulfur	Sulfate Sulfur	Pyritic Sulfur	Organic Sulfur	pH
				%				%			
GC-1	1	7.0-11.0	0.23	0.14	<0.01	0.09	100	61	---	39	3.8
	2	11.0-12.6	0.83	0.37	0.04	0.42	100	45	5	50	3.7
	3	12.6-16.4	0.32	0.13	0.07	0.12	100	41	22	37	3.6
	4	16.4-24.0	0.84	0.10	0.49	0.25	100	12	58	30	5.8
	5	24.0-31.2	0.10	<0.01	0.04	0.06	100	---	40	60	6.2
	6	31.2-34.3	0.18	0.01	0.10	0.07	100	6	56	38	6.5
	7	34.3-39.3	0.24	<0.01	0.14	0.10	100	---	58	42	5.9
	8	39.3-45.0	0.12	0.01	0.04	0.07	100	8	33	59	6.6
	9	45.0-52.0	0.33	0.09	0.14	0.10	100	27	43	30	4.6
	10	52.0-56.9	0.53	0.02	0.38	0.13	100	4	72	24	5.7
GC-2	1	12.0-16.0	0.26	0.20	<0.01	0.06	100	77	---	23	3.8
	2	16.0-26.4	0.09	0.03	0.01	0.05	100	33	11	56	4.4
	3	26.4-31.9	0.07	0.03	<0.01	0.04	100	43	---	57	4.8
GC-3	1	5.0-9.0	0.19	0.14	0.01	0.04	100	74	5	21	3.7
	2	9.0-10.6	0.29	0.23	0.01	0.05	100	79	3	17	4.1
	3	10.6-14.0	0.51	0.36	0.06	0.09	100	71	12	17	3.3
	4	14.0-18.1	0.55	0.28	0.21	0.06	100	51	38	11	3.8
	5	18.1-21.2	0.39	0.14	0.17	0.08	100	36	44	20	5.6
	6	21.2-29.0	0.58	0.05	0.41	0.12	100	9	71	20	5.3
	7	29.0-32.0	0.77	0.10	0.53	0.14	100	13	69	18	5.5
	8	32.0-35.0	0.77	0.01	0.61	0.14	100	2	80	18	5.3
GC-4	1	10.0-14.0	0.07	0.02	<0.01	0.05	100	29	---	71	4.8
	2	14.0-21.7	0.04	<0.01	<0.01	0.04	100	---	---	100	4.9
	3	21.7-23.0	0.29	0.21	0.01	0.07	100	72	3	25	3.6
	4	23.0-29.3	0.04	0.01	0.02	0.01	100	25	50	25	4.4
	5	29.3-31.3	0.22	0.12	0.07	0.03	100	55	32	13	4.7
	6	31.3-35.0	0.12	0.07	0.01	0.04	100	58	8	33	4.5
	7	35.0-36.0	0.28	0.12	0.08	0.08	100	42	29	29	5.3
	8	36.0-42.3	0.12	0.05	0.03	0.04	100	42	25	33	4.7
	9	42.3-48.3	0.41	0.07	0.22	0.12	100	17	54	29	6.1
	10	48.3-50.4	0.09	0.04	0.01	0.04	100	44	12	44	5.2
GC-5	1	8.0-12.0	0.05	<0.01	<0.01	0.05	100	---	---	100	7.6
	2	12.0-22.0	0.05	<0.01	0.01	0.04	100	---	20	80	7.5
	3	22.0-32.2	0.06	<0.01	0.02	0.04	100	---	33	67	7.5
	4	32.2-46.0	0.06	0.02	<0.01	0.04	100	33	---	67	7.3
	5	46.0-57.7	0.05	<0.01	0.01	0.04	100	---	20	80	7.4
GC-6	1	4.0-8.0	0.37	0.28	0.01	0.08	100	76	3	21	3.7
	2	8.0-9.4	0.78	0.68	<0.01	0.10	100	87	---	13	3.5
	3	9.4-10.2	0.27	0.22	<0.01	0.05	100	81	---	19	3.8
	4	10.2-19.6	0.35	0.25	0.03	0.07	100	71	9	20	4.1
	5	19.6-27.3	0.27	0.11	0.09	0.07	100	41	33	26	5.9
	6	27.3-30.1	0.14	0.04	0.04	0.06	100	29	29	42	6.5
	7	30.1-35.9	0.27	<0.01	0.19	0.08	100	---	70	30	7.3
GC-7	1	3.0-7.0	0.04	<0.01	0.03	0.01	100	---	75	25	7.0
	2	7.0-16.0	0.05	<0.01	0.02	0.03	100	---	40	60	5.2
	3	16.0-24.0	0.04	0.03	<0.01	0.01	100	75	---	25	6.5
GC-8	1	4.0-8.0	0.51	0.38	0.04	0.09	100	75	8	17	3.5
	2	8.0-12.8	0.33	0.26	0.01	0.06	100	79	3	18	3.7
	3	12.8-13.9	0.06	0.02	<0.01	0.04	100	33	---	67	5.0
	4	13.9-19.0	0.23	0.15	0.01	0.07	100	65	4	31	7.0
	5	19.0-24.0	0.25	0.09	0.09	0.07	100	36	36	28	7.1



DATE OF SPOILING

GC—1	1975 — 1977
GC—3	1965 — 1970
GC—8	1960 — 1965
GC—6	1955 — 1960
GC—4	1950 — 1955

FIGURE 1. SULFUR FORMS IN SPOIL CORES FROM ABANDONED LIGNITE MINE SPOIL.

total sulfur forms). The trend is general, but there are exceptions, such as sample 9 (45.0-52.0 ft.) which has an anomalously higher sulfate sulfur content.

Associated with this trend is a secondary trend from low pH values (pH 3.6 for sample 1) in the near-surface samples to higher pH values (pH 5.8 in sample 4) in the deeper samples (fig. 1). Spoil core GC-1 shows a trend in acidity from pH 3.8 [sample 1 (7.0-11.0 ft)] decreasing to pH 3.6 [sample 3 (12.6-16.4 ft)] and increasing to pH 5.8 [sample 4 (16.4-24.0 ft)].

A similar trend can be observed in spoil core GC-3 (fig.1) which has a pH value of 3.7 in near-surface spoil [sample 1 (5.0-9.0 ft)] which decreases with depth to pH 3.3 [sample 3 (10.6-14.0 ft)] and finally increases to pH 5.6 [sample 5 (18.1-21.2 ft)] at still greater depth. Similar trends can also be seen in cores GC-4, GC-6, and GC-8, although not so clearly.

A third trend becomes apparent when the pH change is compared to the relative percentage of sulfate sulfur. In spoil core GC-1, pH values as low as 3.6 occur in a sample with sulfate sulfur proportions of 41%; in spoil core GC-3 a pH value of 3.8 occurs at a sulfate sulfur proportion of 51%; and in spoil cores GC-4, GC-6, and GC-8, pH values less than 4.0 are associated with proportions of sulfate sulfur greater than 70%.

The first trend indicates that, even in spoil material which has been mixed by regular dragline side-casting, a vertical sequence in the proportion of sulfate sulfur to pyritic sulfur becomes established within approximately 10 years (e.g. spoil core GC-1). The results indicate that the highest proportions of sulfate sulfur to pyritic sulfur occur within the near-surface spoil and the ratio decreases with depth to the point where there is little or no sulfate sulfur. In the 10-year-old spoil at GC-1, the absence of sulfate sulfur occurs at a depth of approximately 24 ft.; in spoil core GC-3 (20 years old), this point is reached at a depth of approximately 29 ft.; in spoil core GC-6 (30 years old) at over 30 ft.; and in spoil core GC-4 (35 years old) at over 48 ft.

These depths are based solely on the proportions of sulfur forms and may be misleading because they do not take into account the effects of leaching. An appreciable sulfate sulfur content at a depth in the spoil may represent the in-place sulfate generated from pyritic sulfur oxidation, or it may represent the sulfate leached from the overlying spoil column above into a zone in which no significant pyrite oxidation has occurred, or it may represent a combination of both processes.

To determine the significance of leaching in the distribution of sulfate sulfur, the pH of the spoil may be used as an indicator of pyritic sulfur oxidation. For example, in spoil core GC-1, the low pH values (less than pH 4.0) in sample 1 (7.0-11.0 ft), sample 2 (11.0-12.6 ft), and sample 3 (12.6-16.4 ft) are indicative of active pyritic sulfur oxidation. The sample below sample 3 [sample 4 (16.4-24.0 ft)] shows a value of pH 5.8, suggesting that oxidation has scarcely commenced. Similarly, based on pH values in spoil core GC-3, active oxidation of pyrite appears to be occurring to a depth of 18.1 feet (sample 4 - pH 3.8). The next lower sample (sample 5) has a pH value of 5.6. In spoil core GC-8, the transition to higher pH values occurs below 13.9 ft; in spoil core GC-6 below 19.6 ft; and in GC-4 below 23.0 ft (although the distinction is not clear in this case).

If pH transitions are compared to the sulfate sulfur proportions, there appears to be a relationship that varies consistently with the age of the spoil. For example, the 10-year-old spoil in core GC-1 has a pH transition zone associated with a sulfate sulfur proportion of approximately 40%; the 20-year-old spoil in core GC-3 has a pH transition zone associated with a sulfate sulfur proportion of approximately 50%; and the spoil which is over 25 years old in cores GC-8, GC-6, and GC-4 has a pH transition zone associated with a sulfate sulfur proportion of over 70%.

If leaching of sulfate had occurred to any significant degree, then the greatest depletion of sulfate would be expected in the near-surface spoil samples where rainfall leaching would be most intense. Such a depletion of sulfate would be marked on the triangular graphs by an upswing of the near-surface spoil samples towards the organic sulfur apex, since these samples are also depleted in pyritic sulfur as shown earlier. Such trends are indeed exhibited by the older spoils. Spoil core GC-4, representing material that is over 30 years old, shows the first two samples [sample 1 (10.0-14.0 ft.) and sample 2 (14.0-21.7 ft.)] with no pyritic sulfur contents and very low sulfate sulfur contents. Similarly, spoil core GC-8 shows a near-surface sample [sample 3 (12.8-13.9 ft.)] with no pyritic sulfur content and a moderately low (33%) sulfate sulfur content.

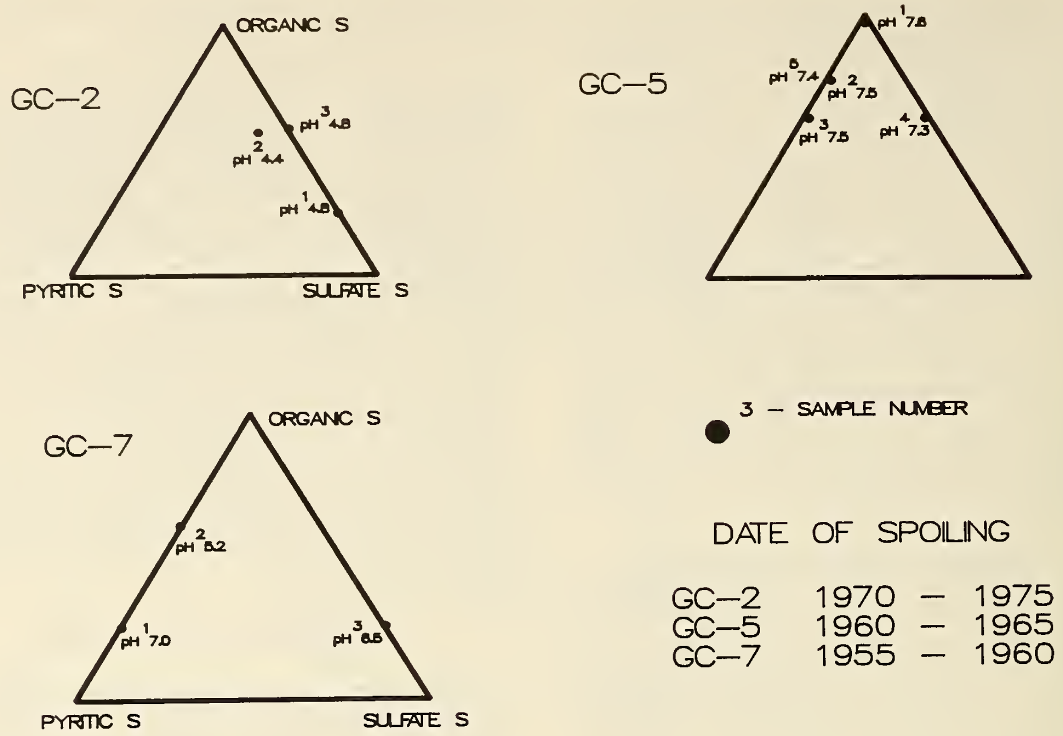
The spoil samples depleted of both pyritic sulfur and sulfate sulfur exhibit pH values that are higher than those associated with active oxidation of pyritic sulfur. In spoil core GC-4, sample 1 (10.0-14.0 ft) shows a value of pH 4.8 and sample 2 a value of pH 4.9; in spoil core GC-8 sample 3 (10.6-14.0 ft) shows a value of 5.0. These pH levels indicate that either pyritic sulfur oxidation never occurred (because no pyritic sulfur was present in that depth interval) or that it has gone to completion and the original low pH has been raised by subsequent base resaturation.

The distribution of sulfur forms in three other spoil cores provides further information on different geochemical conditions to those already described (fig. 2). Spoil cores GC-2 and GC-7 have very low overall total sulfur contents and the sulfur forms were determined near the level of detection. Very small variations in content in any of the sulfur forms are therefore reflected in a very wide scatter on the triangular graphs. With the exception of sample 1 in spoil core GC-2, these cores do not show significant reductions in pH due to pyritic sulfur oxidation. Spoil core GC-5 is atypical in that it displays a combination of very low total sulfur contents and high pH values (above pH 7.0) due to the probable presence of carbonates. The absence of pyritic sulfur and sulfate sulfur results in a cluster of data points on the triangular graph near the organic sulfur apex.

SUMMARY AND CONCLUSIONS

A number of general trends in the area associated with the age of the spoil can be observe that can be attributed to processes of sulfide oxidation and leaching. These may be examined using the proportions of the three sulfur forms (organic sulfur, pyritic sulfur and sulfate sulfur) and pH. From the available data, the hypothetical evolution of the spoil geochemistry in the vadose zone is reconstructed as follows:

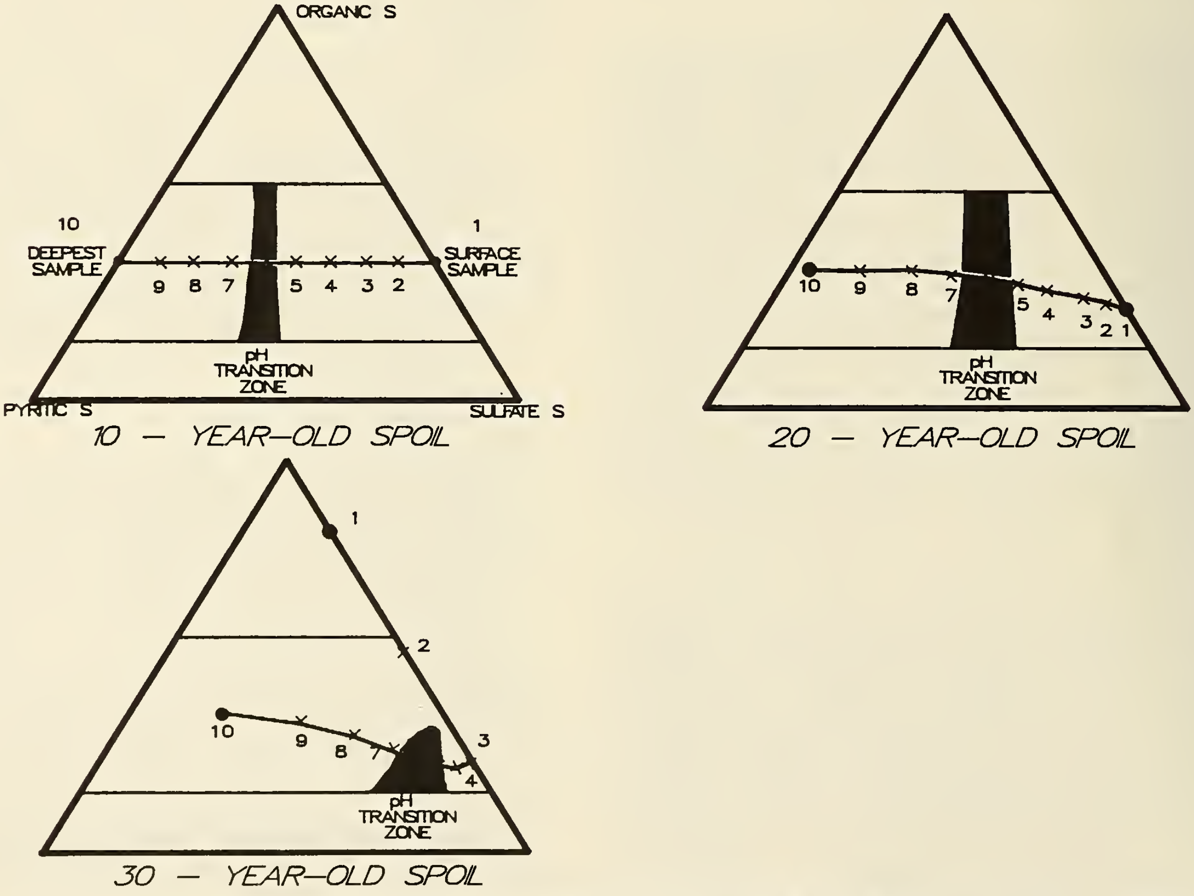
- ° In 10-year-old spoil (fig. 3) there would be a relatively clear sequence of samples with decreasing sulfate sulfur contents and increasing pyritic sulfur contents from the surface down. A transition zone would be observed in which there is a marked pH increase downwards from values less than 4.0 (indicating active and full oxidation of pyritic sulfur) to values greater than 5.0 (indicating that oxidation of pyritic sulfur is, at best, commencing).
- ° After 20 years, the same samples would show a number of changes on the triangular graph. Since a large proportion of pyritic sulfur would have been oxidized, the entire string of data would be drawn closer to the sulfate sulfur apex. The pH transition zone would spread and would be less well-defined. Penetration of oxygen in the vadose zone would have allowed some oxidation of pyritic sulfur even in the deepest sample (No. 10) producing some sulfate sulfur. Some of the sulfate values in the lowermost samples might also represent accumulations of material leached from above.



DATE OF SPOILING

GC–2	1970 – 1975
GC–5	1960 – 1965
GC–7	1955 – 1960

FIGURE 2. SULFUR FORMS IN SPOIL CORES FROM ABANDONED LIGNITE MINE SPOIL


ORGANIC S
10
DEEPEST SAMPLE
1
SURFACE SAMPLE
9 8 7 5 4 3 2
pH TRANSITION ZONE
PYRITIC S
SULFATE S
10 9 8 7 5 4 3 2 1
pH TRANSITION ZONE
1
2
10 9 8 7
3
4
pH TRANSITION ZONE

10 — YEAR–OLD SPOIL

20 — YEAR–OLD SPOIL

30 — YEAR–OLD SPOIL

FIGURE 3. RECONSTRUCTED EVOLUTION OF SULFUR FORMS IN SPOIL CORES

- After 30 years, even more oxidation would have occurred and the top 5 samples would show the pyritic sulfur proportion to be less than 10% of the total sulfur forms. The pH transition zone would be very diffuse and difficult to define although it would be closer to the sulfate sulfur apex. Leaching of sulfate from the surface samples would have been significant.

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THE RATE OF OXIDATION OF PYRITES FROM COAL AND ORE SOURCES - AN AC IMPEDANCE STUDY[1]

S. Chander and A. Briceno[2]

Abstract.--The rate of oxidation of pyrites from coal and mineral sources has been determined using a new technique of AC impedance spectroscopy. In this technique the impedance of the pyrite/solution interface is measured as a function of frequency from which the charge transfer resistance can be calculated. From the charge transfer resistance the rate of oxidation is calculated using the Stern-Geary equation. The results show that the rate of oxidation of the pyrite sample from a coal source is substantially greater than the corresponding rate of oxidation of the pyrite sample from an ore source. The charge transfer resistance of the ore pyrite increases with the extent of oxidation whereas the coal pyrite showed no such increase. In the case of ore pyrite the surface film acts as a passivating layer and retards the rate of oxidation. The formation of a protective film on coal pyrite is not observed.

RATE OF PYRITE OXIDATION AND ACID MINE DRAINAGE

The pollution of mine waters by acids generated through oxidation of pyrite is a well recognized problem, particularly for the coal industry. Although the potential for acid mine drainage (AMD) depends on a variety of factors which include sulfide content, sulfide form, sulfide surface area, rock type (acid neutralization capacity), and rock permeability, prediction of the amount of acid generated still remains a difficult task (Caruccio 1968, Barton 1978, Rose et al. 1983). A major factor in the amount of free acid generated is the relative rates of acid generation through oxidation of the sulfide and the rate of acid consumption by the host rock. This is schematically illustrated in figure 1 in which G_1 and G_2 refer to two different rates of acid generation and C_1 and C_2 refer to two different rates of acid consumption. Clearly, the amount of acid generated, shown by the hatched area, is substantially greater for (G_1, C_1) conditions than it is for (G_2,C_2) conditions even though the total amount of sulfide is the same. Thus, one approach to decrease the AMD problem is to reduce the rate of oxidation of pyritic minerals. However, this approach requires an understanding of the factors that determine the rate of pyrite oxidation.

The importance of the rate of oxidation of pyrite in AMD has been recognized by many investigators (Singer

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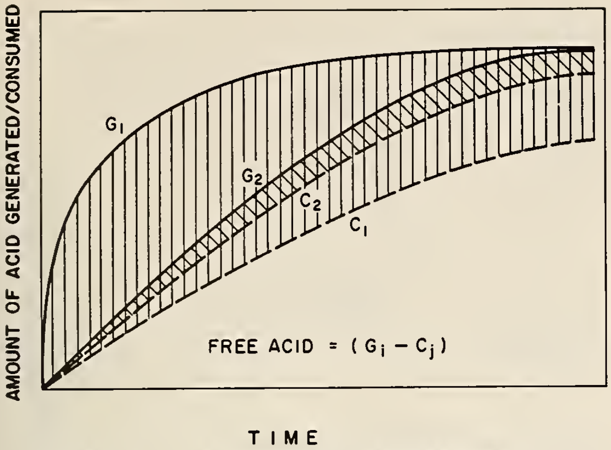

Figure 1.--A schematic representation of the amount of acid generated (G_1 or G_2) by oxidation of sulfides and the amount of acid consumed (C_1, C_2) by the host rock. The hatchured areas represent the amount of acid generated for two sets of conditions: ▥ - (G_1, C_1) and ▧ - (G_2, C_2).

and Stumm 1970, McKibben 1984), but the techniques for studying oxidation rates and the conditions of investigation vary considerably. The rates have been determined by:

1) Measurements of the amount of acid generated (represented as acidity in $CaCO_3$ equivalent);

2) Measurements of iron species in solution as Fe^{2+} and Fe^{3+};

3) Measurements of sulfur species in solution as $SO_4^=$, $S_xO_y^=$, etc;

4) Measurements of changes in pH or free H^+ concentration in solution;

5) Measurements of Eh of slurry which is a measure of Fe^{3+}/Fe^{2+}, P_{O_2}, etc. in solution;

6) Analysis of solid oxidation products (possible only when substantial fraction of pyrite has oxidized).

Although each of these techniques gives a measure of the rate of oxidation, the results cannot be directly related because pyrite oxidation occurs through formation of several intermediate ions like ferrous, ferric, thiosulfate, dithionate, etc.; and solid products like elemental sulfur, ferrous and ferric hydroxides, geothite, lepidocrocite, maghemite, and hematite. The study of the mechanism of pyrite oxidation, particularly in slightly acidic to slightly alkaline solutions, is further complicated by formation of surface coatings of the solid oxidation products. The presence of such oxidation products might change the rate limiting step from the chemical (or electrochemical) reaction

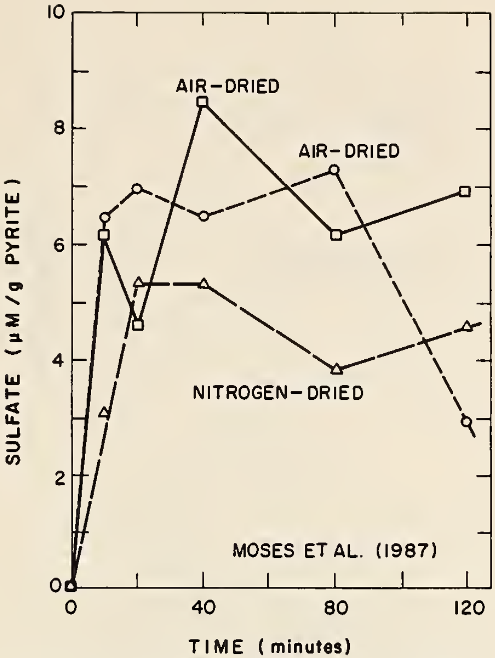

Figure 2.--The amount of sulfate generated by pyrite oxidation in oxygen-saturated solutions at initial pH 9 (Moses et al. 1987).

control to mass transfer control through the product layer. The results of pyrite oxidation reproduced in figure 2 from a recent study (Moses et al. 1987) clearly show that the data are difficult to intepret in terms of a kinetic model. Attempts by other investigators to intepret the simple kinetic data, particularly for oxidation in mild conditions have also met with difficulties (Esposito et al. 1987). This investigation was undertaken to develop a new technique of AC impedance spectroscopy to measure reactivity of the pyrite/solution interface.

AC IMPEDANCE SPECTROSCOPY

The technique of AC impedance spectroscopy to measure reactivity of pyrite is based on measurements of current through a pyrite electrode. The current is directly proportional to the rate of oxidation, which depends upon the potential, E, of the electrode (the potential represents the driving force for oxidation). If a sinusoidal potential,

$$E = \Delta E \sin \omega t$$

is applied, the current through the electrode is

$$i = \Delta i \sin (\omega t + \phi)$$

where ΔE is the amplitude of the AC signal, ω is the angular frequency ($=2\pi f$, where f is the frequency in hertz), Δi is the amplitude of the current, and ϕ is the phase lag. The impedance, Z, is defined as

$$Z = dE/dI$$

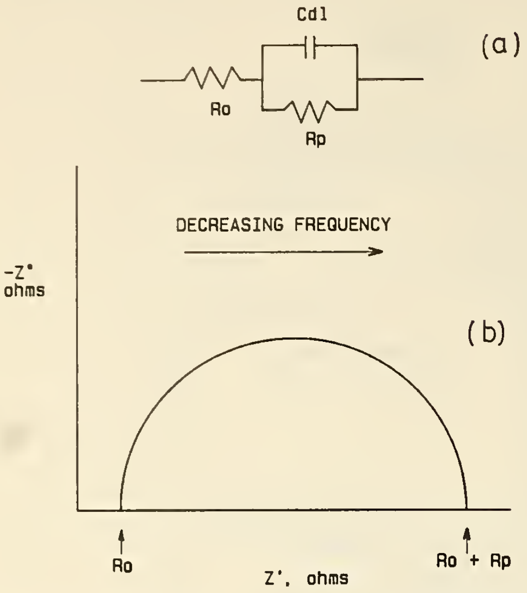

Figure 3.--a) A simple equivalent circuit for pyrite/solution interface. R_p - charge transfer resistance, C_{dl} - interfacial capacitance, and R_o - solution resistance. b) A Nyquist plot of equivalent circuit shown in figure 3a.

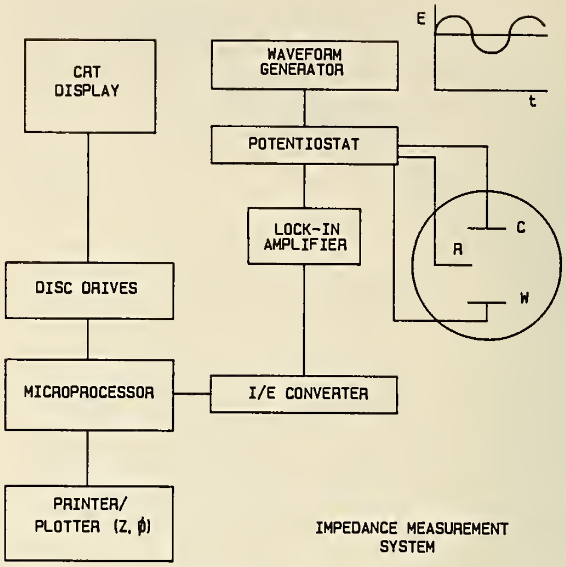

Figure 4.--A schematic of the impedance measurement system. W-working electrode (pyrite), C-counter electrode (graphite), and R-reference electrode.

In general, the impedance consists of a real component, Z', and an imaginary component, Z", such that

$$Z = Z' + jZ''$$

If the pyrite/solution interface is represented by a resistance term, R, and a capacitance term, C,

$$Z' = R,$$

$$Z'' = 1/(\omega C)$$

Ac impedance spectroscopy involves measurements of the impedance as a function of frequency from which the values of R and C can be obtained. A simple equivalent circuit for the pyrite/solution interface is given in Figure 3a where R_p represents the change transfer term for the pyrite/solution interface, C represents the interfacial capacitance, and R_o represents the solution resistance. The results of the impedance measurements can be plotted in the form of a Nyquist plot shown in Figure 3b from which values of R_p can be obtained. The values of R_p obtained for pyrites from different sources are discussed in this paper. The capacitances were also obtained, but will be discussed elsewhere. The rate of oxidation of pyrite, which can be represented as the exchange current density, I_o, is related to the change transfer resistance through the Stern-Geary equation

$$I_o = \frac{1}{2.303R_p} \cdot \frac{b_a b_c}{b_a + b_c}$$

where b_a and b_c are the anodic and cathodic Tafel slopes, respectively.

EXPERIMENTAL METHODS AND MATERIALS

The impedance measurements were made with a Model 368-1 impedance system manufactured by EG&G Princeton Research. It consists of a Model 173 potentiostat and a Model 5706 lock-in amplifier. Both units are operated by an Apple IIe microcomputer through a Model 276 interface. Both the data acquisition and analysis were carried out with the aid of the computer. A typical impedance experiment consisted of the measurement of the magnitude and phase angle of the impedance as a function of frequency. An AC signal of 10 mV in the frequency range of 10^{-3} to $2x10^{4}$ Hz was used in the impedance measurements. A schematic of the electrochemical setup is shown in figure 4. A three-electrode system was used in which the working electrode was a polished specimen of pyrite of 1 cm^2 geometric area. A saturated calomel electrode was used as the reference electrode and two graphite rods were used as the counter electrodes.

The pyrite crystals were cut to size, and the exposed surface of the sample was polished on a 600-grit silicon carbide paper. The samples were polished wet under distilled water and then transferred to the cell quickly after washing. Samples were handled only by gloves during the entire polishing procedure. Although pyrite oxidation could not be prevented by this procedure, alternate chemical treatments were found to be unsatisfactory. The solution was deoxygenated by bubbling purified nitrogen overnight before inserting the sample in the cell. Nitrogen was bubbled throughout the conditioning period, which lasted about three hours unless otherwise stated. During an electrochemical measurement, the flow of nitrogen at the surface of the solution was continued to eliminate diffusion of atmospheric oxygen into the cell.

The ore pyrite sample was from Muro de Aguas, Logrono Province, Spain, and the coal pyrite was from a "sulfur ball" from the Lower Kittaning Seam, PA.

Distilled water from a tin-lined Barnstead still (Model 210) equipped with a Q-baffle system was used in this investigation. Water of specific resistivity greater than 2 Mohm-cm was used in all the experiments, which were conducted at room temperature.

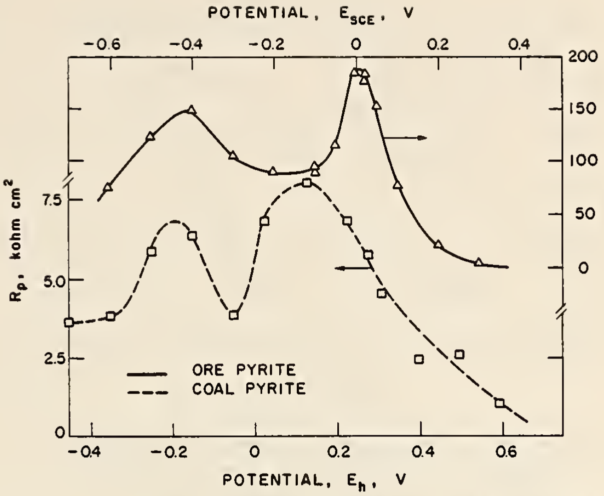

Figure 5.--The charge transfer resistance for an ore and a coal pyrite as a function of the DC potential.

RESULTS AND DISCUSSION

The results of the AC impedance measurements for the coal and ore pyrite samples are presented in figure 5. The charge transfer resistance (R_p) is plotted as a function of the DC potential for the pyrite/solution interface. It is small when the electrochemical reactivity of the interface is large (i.e., large reaction rate) and vice-versa. The results in figure 5 show that the coal pyrite is generally more reactive than the mineral pyrite in the potential range of -0.4 to 0.4 V. The functional dependance of the charge transfer resistance on potential is also different for the two pyrites. The ore pyrite sample shows a maximum in R_p at 0.25 V*. This potential is slightly greater than the rest potential of pyrite, which is 0.19 V. In contrast to this behavior, the coal pyrite shows a maximum in the charge transfer resistance at 0.12 V, which is slightly below the rest potential of coal pyrite (0.28 V). The magnitude of the charge transfer resistance for this pyrite is about 25 times smaller than the corresponding value for the ore pyrite. These results imply that the coal pyrite begins to oxidize at lower potentials than ore pyrite. The exchange current densities obtained by using the Stern-Geary equation are plotted in figure 6 for the pyrites from the coal and the ore sources. The high reactivity of the coal pyrite is clearly seen. The filled symbols are the exchange current densities obtained by steady state polarization measurements.

For the ore pyrite, the charge transfer resistance increases with increase in the extent of reaction as shown in figure 7, in which R_p is plotted as a function of charge transferred. In this series of tests, an anodic charge was passed to oxidize the pyrite under galvanostatic conditions (i.e. constant rate of oxidation), and the AC impedance measurements were carried out after a predetermined amount of charge was passed. The increase in R_p for the ore pyrite shows that a film forms on the surface of pyrite, the resistance of which increases with the amount of charge transferred or extent of the reaction. The film acts as a passivating layer and retards the rate of oxidation. A passivating film does not form on the surface of the coal pyrite, however. The results for coal pyrite, in figure 7, show that the charge transfer resistance does not increase with charge transferred. The coal pyrite continues to oxidize rapidly due to the absence of a protective film.

The nature of product layers on the surface of the reacted pyrites can be schematically represented as shown in figure 8. The product layer is relatively nonporous (or dense) at the surface of the ore pyrite (fig. 8a), whereas it is highly porous at the surface of the coal pyrite (fig. 8b).

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*The impedance measurements on ore samples from alternate sources show a similar behavior with the exception that the magnitude of the charge transfer resistance is different for each pyrite. The charge transfer resistance correlates very well with the oxidation behavior also. These results are published elsewhere (Chander and Briceno 1987).

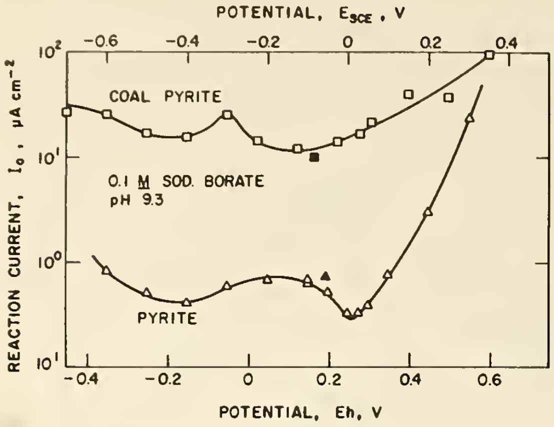


Figure 6.--The reactivities of pyrites from two different sources as a function of the DC potential.

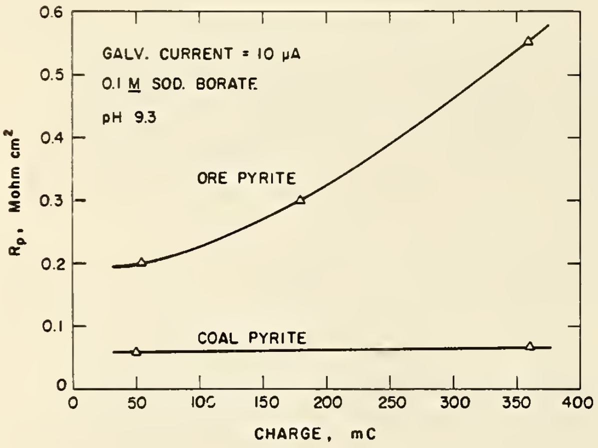
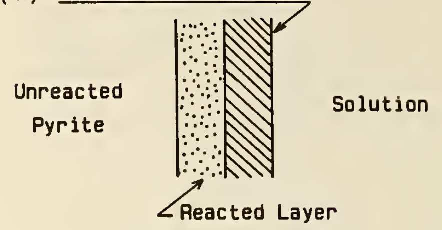


Figure 7.--The charge transfer resistance of ore and coal pyrites as a function of the extent of reaction (measured in terms of charge transferred).

(a) **Uniform Product Layer**



(b) **Non-uniform Product Layer**

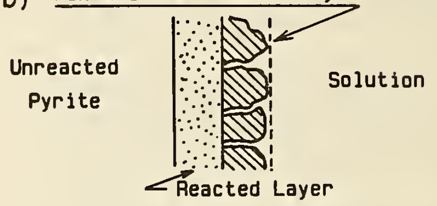


Figure 8.--A schematic representation of surface layers on pyrite.

Further analysis of the impedance data with the aid of a two-layer model (Chander et al. 1988) shows that the resistance of the coal pyrite/solution interface is primarily a charge transfer resistance (i.e., resistance of the porous film is negligible), whereas the resistance of the ore pyrite/solution interface consists of a charge transfer term for the product layer. Although the reasons for formation of a passivating film on the ore pyrite or the lack of a passivating film on the coal pyrite are not entirely clear, it is believed that the micropores in coal pyrite play an important role. For coal pyrite the dissolution occurs inside the pores or microcracks whereas precipitation of the product occurs outside the mouth of the micropore or crack. The product layer is sufficiently porous to allow diffusion of reactants and products. The conditions which give rise to a change in the characteristics of the product layer can significantly alter the rate of pyrite oxidation. Additional studies are needed to determine the nature of surface films that form on the surface of pyrites and the role they play in pyrite oxidation phenomena.

SUMMARY

A new technique of AC impedance spectroscopy has been developed to determine the rate of oxidation of pyrite. This technique is especially useful for studying the reactivity of solids when product layers form at the interface. The study of oxidation of an ore pyrite, which is a hydrothermal pyrite, shows that a protective film forms on the surface of pyrite which retards the rate of reaction. In contrast, the microporous nature of coal pyrite, which is a brackish-water pyrite, gives rise to a nonproductive (highly porous) product layer.

ACKNOWLEDGEMENTS

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A QUANTITATIVE ASSESSMENT OF THE NATURAL ABATEMENT OF ACID MINE DRAINAGE BY INTERACTION WITH ALLEGHENY GROUP LITHOLOGIES

Andrew D. Stahl and Richard R. Parizek[1]

Abstract.--Acid mine drainage is produced by the oxidation of iron sulfide minerals in the presence of air and water. Once this drainage enters a saturated ground-water system, oxidation is inhibited by the absence of air. The aquifer minerals will not be in equilibrium with the acid water and one or more reactions may proceed which results in acid drainage amelioration. In order to predict the rate and direction of migration of acid drainage contaminants within ground water, it is essential to be able to quantify the natural abatement capacity of the mine drainage affected rock. A laboratory procedure has been developed which may quantify the "acidity distribution coefficient" of acid mine drainage contaminated aquifers in which flow is dominated by fracture porosity. This technique is a modification of the batch adsorption tests commonly used to describe ion-exchange and adsorption reactions in porous media. All mathematical models which describe the transport of a reactive contaminant must employ the distribution coefficient. For aquifers in which ground-water flow occurs primarily through fractures rather than intergranular pores, the distribution coefficient is a measure of the amount of contaminant adsorbed by the aquifer per surface area of rock exposed to the solution. Lower and Middle Kittanning cores, drill cuttings, and strip mine highwall samples have been analyzed for their capacity to ameliorate acidic solutions. All laboratory batch tests resulted in an increase in pH, regardless of the rock sample's acid-base account. All samples without carbonate material and with a low sulfur content were found to have a significant acid consuming capacity. All samples with an acid-base account greater than -40 (tons $CaCO_3$ equivalent per thousand tons of material) consumed acidity in the batch experiments. Some samples with an acid-base account greater than -140 but less than -40 consumed acidity in the batch tests. Field tracer

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tests are another way of obtaining values for reactive contaminant transport parameters. Small scale acid-injection tests have been performed in wells from which the drill cuttings have been collected. The results of these tests illustrate that the developed laboratory technique has potential for predicting field occurrences.

INTRODUCTION

Acid mine drainage is produced by the oxidation of iron sulfide minerals in the presence of air and water. Once this drainage enters a saturated ground-water system, oxidation is inhibited by the absence of air. The aquifer minerals will not be in equilibrium with the acid water, and one or more reactions may proceed which results in acid drainage amelioration. All mathematical models which describe the rate and direction of migration of a contaminant that chemically interacts with the medium through which it flows must employ a parameter termed the "retardation factor". A reactive contaminant, such as acid mine drainage, will migrate at a rate slower than that of the surrounding ground water. The retardation factor is a measure of the difference between these two flow velocities. Such delays in the transport of acid mine drainage have been noted in western Pennsylvania aquifers. Prior to the research presented in this paper, there had been no serious attempt to quantify acid drainage transport parameters. Hence, the ability to predict the migration of acid mine drainage within soils, aquifers, and confining beds had been very poor.

Reactive Contaminant Transport Parameters

Much work has been conducted in quantifying the retardation of reactive contaminants other than those relating to acid mine drainage. These analyses most often involve the determination of the distribution coefficient (K_d). As discussed by Freeze and Cherry (1979), in systems dominated by intergranular flow, the definition of the distribution coefficient and its relation to the retardation factor (R) are described by the equations:

K_d = (mass of solute on the solid phase per unit mass of solid phase) / concentration of solute in solution

R = 1 + (bulk density/porosity) * K_d

The method most often employed for K_d measurement is the laboratory batch experiment. These tests are performed by placing crushed rock in contact with a contaminated solution. The mixture is agitated on a shaker until equilibrium is reached. The effluent is then withdrawn and analyzed for the amount of contaminant retained by the rock. Knowing the initial and final solute concentrations, the volume of the solution, and the mass of the dry rock, the K_d can then be calculated (Pickens et al. 1981). Another approach for K_d measurement is the field tracer test. This test is conducted by injecting the contaminated solution into a formation via a drillhole. After a certain amount of contact time with the rock, water samples are then collected and analyzed for the amount of contaminant retained by the formation.

For systems dominated by fracture flow, Burkholder (1976) defines the distribution coefficient (K_a) and the retardation factor:

K_a = (mass of solute on solid phase per unit area of solid phase) / concentration of solute in solution

R = 1 + (ratio of surface area to void space * K_a)

Previous Work

The majority of previous work relating to chemical changes of acid mine drainage has been concerned with the effectiveness and practicality of various acid drainage treatment procedures. However, more closely related to the research presented in this paper, Crouse and Rose (1976) analyzed the natural ameliorative processes occurring in an acid mine drainage affected stream. They concluded that the stream sediments effected beneficiation by consuming hydrogen ions as a result of cation-exchange reactions and reactions with primary and secondary silicates. Ciolkosz et al. (1973) conducted soil percolation experiments and laboratory batch tests to analyze the ability of soils to renovate acid mine water. They discovered that maximum effect on pH, total acidity, conductivity, and iron content of the solution occurred within five minutes and in a 1:1 solid to solution ratio. They batch tested 21 Pennsylvania soils and learned that most of the variation of pH, total acidity, and iron were accounted for by cation-exchange capacity and $CaCO_3$ equivalent.

A time-distance acid-front migration finite element analysis is incorporated into the GEOFLOW model of D'Appolonia Waste Management Services, Inc. (Haji-Djafari 1983). The determination of the acidity retardation factor in this model is based only on the neutralization capacity of the porous media. Through a conversation with one of the GEOFLOW modelers it was learned that much difficulty exists in obtaining reliable results with this acid-transport routine (Snyder 1986). A discussion exists within the GEOFLOW user's manual suggesting the use of laboratory test data "to simulate acid-front migration and variations in solute retardation factors".

Research Objectives

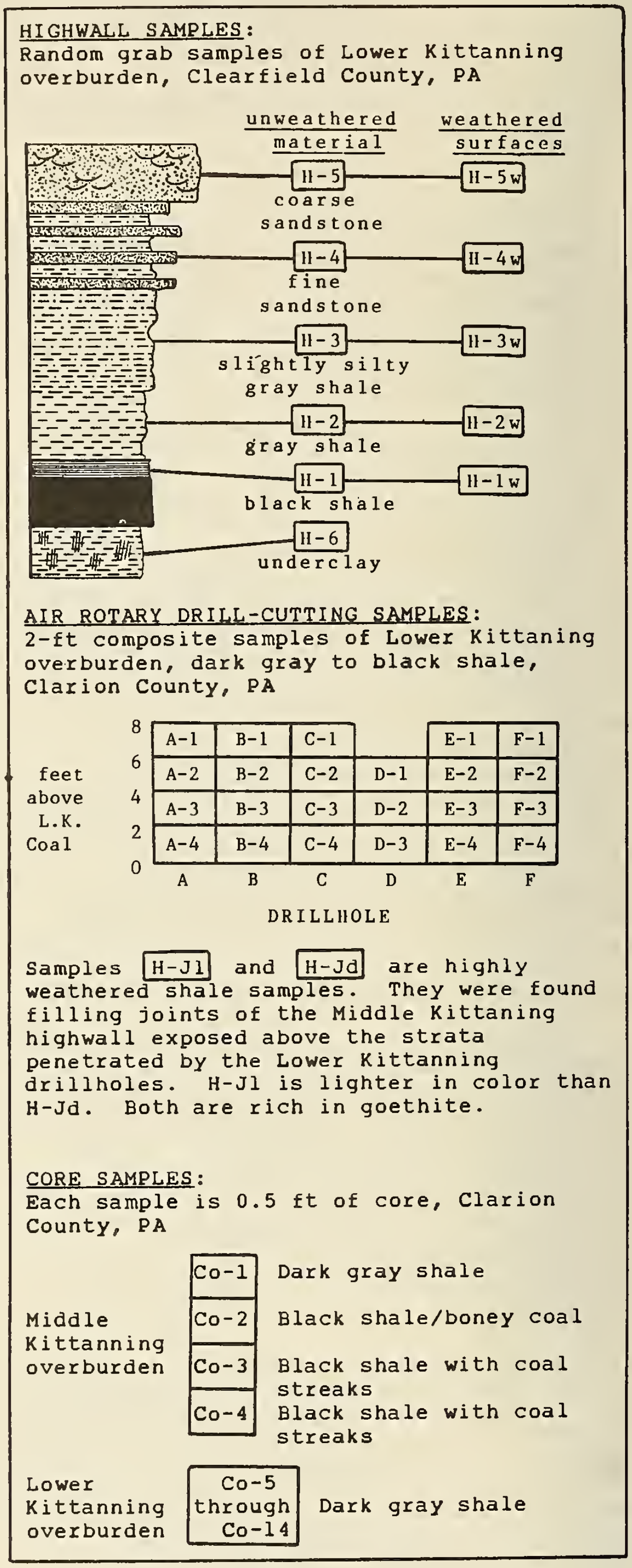
One goal of this research is to determine whether a lithology completely lacking carbonate material, or otherwise possessing a negative acid-base account as determined by Environmental Protection Agency procedures (Sobek et al. 1978), can nevertheless consume acidity through ion-exchange and surface adsorption reactions.

This question was addressed with the development of a laboratory procedure derived from the batch adsorption tests commonly used to describe ion-exchange and adsorption reactions in porous media (Relyea et al. 1980). Upon establishment of a reproducible batch test experimental method, the nature of contaminant transport in coal measure strata was considered. It has been observed that much ground-water flow in the coal measures of western Pennsylvania occurs in rock with very little if any intergranular porosity. The main avenues for ground-water movement in these fracture-dominated flow systems are joints and bedding plane partings in which acid abatement reactions are limited by the available surface area of the fractures and the mineralogy exposed on these surfaces. For these reasons, both weathered and unweathered rock have been analyzed, and available surface area is a controlled parameter in the developed laboratory batch technique. Through additional research it is hoped that this laboratory procedure will be modified into a valid procedure for quantification of the natural acid abatement processes occurring in a fracture-dominated flow system.

DESCRIPTION OF RESEARCH

Rock Sample Collection and Preparation

Figure 1 describes each rock sample used in the laboratory batch experiments. Weathered surfaces were broken off of the highwall samples and treated as separate samples. All samples except the drill cuttings were crushed by a jaw crusher. Representative splits were taken from each sample; part of the split was used for cation-exchange capacity tests. The rest of the split was pulverized for analyses including neutralization potential, maximum potential acidity, x-ray diffraction, and carbonate carbon content. In preparation for the batch experiments, the material not part of these splits was separated into size fractions by mechanical sieving with a nested sieve series and



AIR ROTARY DRILL-CUTTING SAMPLES:
2-ft composite samples of Lower Kittaning overburden, dark gray to black shale, Clarion County, PA

feet above L.K. Coal	A	B	C	D	E	F
8–6	A-1	B-1	C-1		E-1	F-1
6–4	A-2	B-2	C-2	D-1	E-2	F-2
4–2	A-3	B-3	C-3	D-2	E-3	F-3
2–0	A-4	B-4	C-4	D-3	E-4	F-4

DRILLHOLE

Samples H-Jl and H-Jd are highly weathered shale samples. They were found filling joints of the Middle Kittaning highwall exposed above the strata penetrated by the Lower Kittanning drillholes. H-Jl is lighter in color than H-Jd. Both are rich in goethite.

CORE SAMPLES:
Each sample is 0.5 ft of core, Clarion County, PA

Middle Kittanning overburden	Co-1	Dark gray shale
	Co-2	Black shale/boney coal
	Co-3	Black shale with coal streaks
	Co-4	Black shale with coal streaks
Lower Kittanning overburden	Co-5 through Co-14	Dark gray shale

Figure 1.--Description of rock samples used in laboratory batch experiments.

shaker. X-ray diffraction analyses were performed on different size fractions of highwall samples H-2; the material retained on sieve #4 was pulverized and its x-ray pattern was compared to that of the particles passing sieve #100 and the pattern of the initial representative split. All three patterns indicate identical mineralogy.

Batch Test Procedure

Each sample was analyzed for its natural acid abatement capacity through the following laboratory batch experiment procedure. Rock particles passing the #3 mesh sieve (6.680 mm) and retained on the #4 mesh sieve (4.699 mm) are rinsed in distilled water to remove all silt and clay-sized material. The gravel is then thoroughly dried by compressed air. One hundred grams of the dry particles are placed in a 500 mL Erlenmeyer flask with 100 mL of hydrochloric acid solution (pH = 2.1). The mixture is gently agitated on a wrist-action shaker for 5 hours. The solution is then carefully poured from the rock and its pH, Eh, and temperature are measured. The sample is then filtered, and 50 mL are set aside for total acidity titration. The remaining solution is again measured for pH, Eh, and temperature as well as specific conductance. After these measurements are made the sample is acidified and stored for later analyses of cations and sulfate. At this time the total acidity titration is performed. The rock particles are again rinsed in distilled water, dried, and stored. All water analysis procedures conform to the methods of the U.S. Environmental Protection Agency (1979) and/or the American Public Health Association (1980). The research which led to the development of this laboratory batch test procedure is discussed in the next section.

At this point it should be stressed that at the present stage of research and development, the established laboratory technique can not predict field occurrences. A calibration procedure would need to be developed in order to allow laboratory batch test results to be used in field transport models under variable conditions. The batch experiment procedure described above was derived to yield reproducible results that will address questions such as that stated earlier; i.e., whether lithologies with a negative acid-base account can consume acidity through ion-exchange and adsorption reactions. It is recognized by the authors that a hydrochloric acid solution at a pH of 2.1 does not realistically mimic an acid mine drainage plume. We do feel, however, that this is a logical starting point for continuing research.

Derivation Of The Batch Test Procedure

Highwall samples H-2 and H-3 were used for the trial and error experimentation which resulted in the procedure described above. These samples were chosen after preliminary rock analyses and batch tests produced favorable results. H-2, a gray shale, has no noticeable intergranular porosity. H-3, a slightly silty gray shale, has very little if any intergranular porosity. They were found to have no carbonate carbon and very little sulfur. The batch tests resulted in significant increases in pH and decreases in total acidity and specific conductance.

Many of the preliminary batch experiments were devoted to the careful control of available rock surface area. One major problem was prevention of particle abrasion and rounding during the contact time. As expected, there was a direct relationship between the decrease in acidity and the amount of mud generated by abrasion. A very specific agitation level was found to be ideal for preventing abrasion; the shaking intensity on the wrist-action shaker was adjusted so that the solution remained slightly turbulent while the rock particles remained stationary. Also contributing to the available surface area are silt and clay-sized particles adhering to the larger particles. It was feared that briefly rinsing the particles in distilled water might cause desorption of ions thereby artificially creating adsorption sites. However, batch tests conducted without rinsing resulted in a greater decrease in acidity than tests conducted with rinsing; the exposed surface area of the fine particles consumed more acidity than did artificially created adsorption sites. Therefore, in evaluating the amount of acidity consumed per unit surface area of rock, not rinsing the particles introduces more error than does rinsing. It was learned that drying the rinsed particles with heat caused them to become brittle and very easily abraded. Drying with compressed air caused no such problem.

Once the above problems were resolved numerous batch tests were conducted on H-2 and H-3 in order to determine a contact time, particle size, and initial solution concentration that would be reasonable and would yield a reproducible batch test procedure. The established values have been mentioned above.

As discussed earlier, numerous rock and water analyses have been performed. However, considering the scope of this paper and space limitations, much of these data are excluded and will be published in the near future. This includes, in particular, cation-exchange capacities of rock samples, and batch-test solution sulfate and cation concentrations. The only data discussed in this paper are of those parameters found in table 1. Furthermore, the geochemical reactions and their kinetics deserve a much more elaborate discussion than can be presented here.

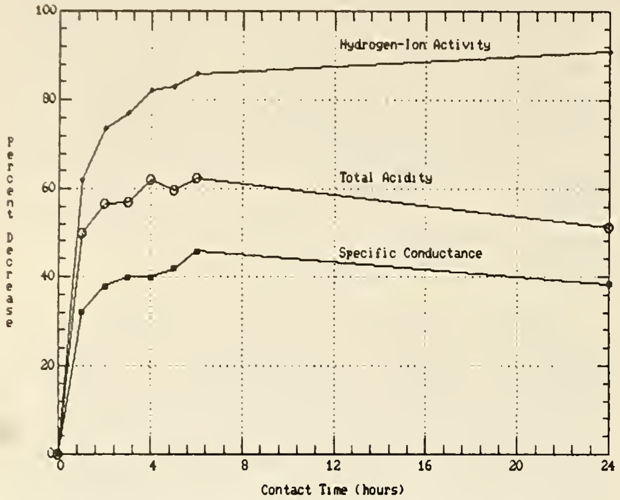


Figure 2.--Change in chemistry versus contact time, sample H-2.

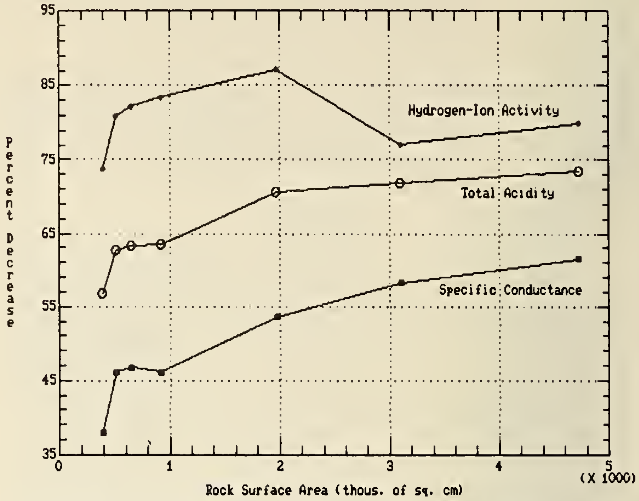


Figure 4.--Change in chemistry versus rock surface area, sample H-2.

Figures 2 and 3 illustrate the change in chemistry versus contact time for H-2 and H-3 respectively. Particles retained on the #4 mesh sieve were equilibrated with a hydrochloric acid solution of pH = 2.1 . Batch tests were conducted for 1, 2, 3, 4, 5, 6, and 24 hours. Five hours was chosen as the contact time for the remaining tests. Figure 2 shows the decrease in hydrogen-ion activity continuing after 5 hours (the pH continued to rise). In this case it appears 5 hours is a conservative choice. In contaminant transport considerations it is always better to underestimate the adsorption capabilities of an aquifer rather than overestimate it. A peak in the consumption of total acidity and conductance is indicated at about 6 hours. It may be that oxidation of the small pyrite content of H-2 may eventually become an influencing factor. In natural ground-water systems there is much less available oxygen compared to the oxygen available in these batch adsorption experiments. Therefore, in aquifers, pyrite oxidation is usually limited or prevented. Data supporting this statement are presented later. As will also be discussed later, the occurrence of pyrite oxidation in the batch test versus in the aquifer is an aspect of this research that needs further investigation. Figure 3 shows a relatively constant pH and specific conductance after 5 hours. The continued consumption of acidity may be related to the slight intergranular porosity that H-3 may possess. Once again, it is more conservative and safe to assume only fracture flow when in actuality, some intergranular flow does occur.

Figures 4 and 5 illustrate the change in chemistry versus rock surface area exposed for H-2 and H-3 respectively. The rock was equilibrated with a hydrochloric acid solution of pH = 2.1 . Batch tests were conducted for particles retained on mesh numbers 4, 5, 7, 10, 20, 30, and 45. The x-axis scale of these figures is thousands of cm². This surface area was calculated assuming the particles to be

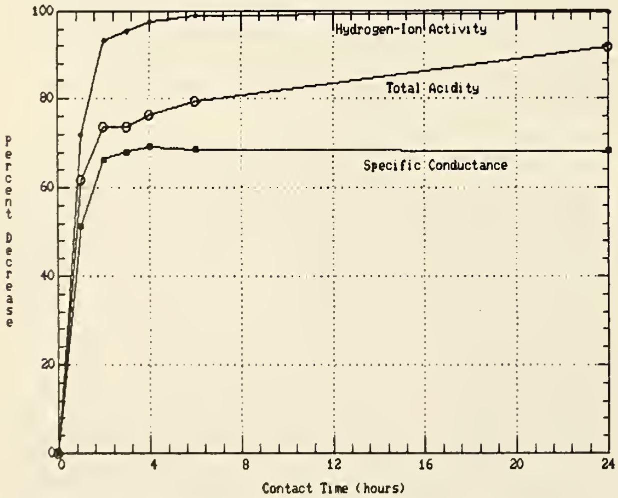


Figure 3.--Change in chemistry versus contact time, sample H-3.

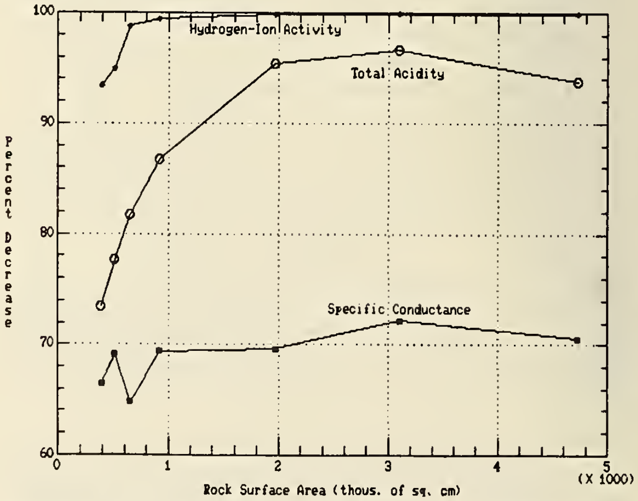


Figure 5.--Change in chemistry versus rock surface area, sample H-3.

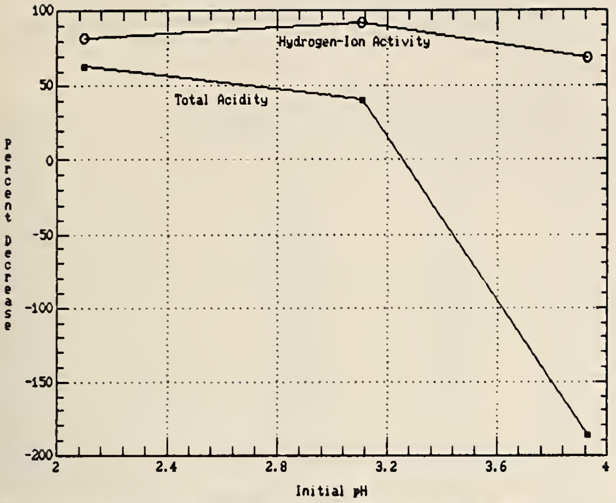


Figure 6.--Change in chemistry versus initial solution pH, sample H-2.

spheres of diameter equal to the average of the mesh sizes of the sieve on which the particle was retained and the sieve the particle last passed. Also assumed was an average density of 2.7 g/cm³. In almost all cases consumption of acidity, hydrogen ions, and conductance increases with increasing surface area. The choice of the largest particles, those retained on #4 mesh sieve, is the most conservative. It is not clear why H-2 did not continue to increase its consumption of hydrogen ions with increasing surface area.

Figures 6 and 7 illustrate the change in chemistry versus initial concentration of the hydrochloric acid solution for H-2 and H-3 respectively. Rock particles retained on the #7 mesh sieve were equilibrated with the solutions. Batch tests were conducted with initial pH values of 2.1, 3.1, 3.9, and 5.4 . Once again, the y-axis scale is labeled "percent decrease". Negative values indicate levels of total acidity or hydrogen-ion activity greater than the initial solution values. Both H-2 and H-3 consumed a large percentage of hydrogen ions from each of the test solutions. H-3 consumed larger percentages of acidity from the two solutions of higher initial concentration (low pH) than from the solutions of lower initial concentration. The same trend is seen for H-2 (fig. 6). The difference is, however, that H-2 produced acidity when equilibrated with the two solutions of lower concentration. For graphical clarity, the H-2 batch test data with the lowest initial concentration are not presented on figure 6. The test results are an increase of total acidity of 6.5 times and a slight decrease in pH. These data suggest that batch tests conducted with solutions of low initial concentration may not accurately describe field occurrences. As discussed above and below, acid production is suppressed in saturated ground-water systems. Therefore, the solution of highest initial concentration was chosen for the remaining batch experiments.

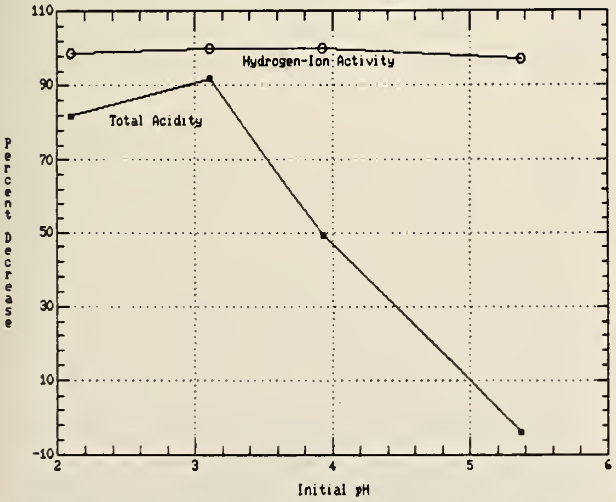


Figure 7.--Change in chemistry versus initial solution pH, sample H-3.

The above discussion indicates the complications involved with using batch test analyses for predicting the total acidity of ground water in an acid drainage-contaminated aquifer. With further research this problem should be better understood. However, the data do not suggest the same problem with hydrogen-ion activity. Although this parameter will continue to be referred to as the "percent decrease in hydrogen-ion activity", it may also be valid to present the results as the "hydrogen-ion distribution coefficient" as discussed in the introductory sections of this paper. Helfferich (1962) discusses the equation, known as the Freundlich isotherm, which describes ion-exchange equilibria. When considering surface area rather than rock mass, the equation can be written:

$$\log S = b \log C - \log K_a$$

where: S = (Initial Concentration - Final Concentration) / Surface Area
C = Final Concentration
K_a = Distribution Coefficient
b = Slope of the log - log Adsorption Relation

In order to calculate the distribution coefficient (K_a) from laboratory batch experiment results, it must be shown that the Freundlich isotherm is such that b=1. Figure 8 shows the linear regression of log S versus log C for hydrogen-ion activity measurements of H-3 batch experiments. The slope of the regression line is 0.93 with a correlation coefficient of 0.89. This suggests that the developed batch test procedure may be valid for quantitative measurement of the hydrogen-ion distribution coefficient. Once again, until more field and laboratory research is conducted, this parameter will continue to be referred to as the "decrease in hydrogen-ion activity".

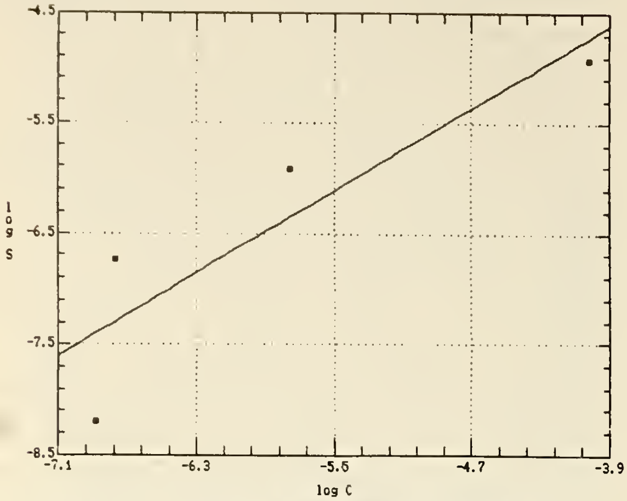


Figure 8.--Log-log adsorption relation with regression line of sample H-3 batch test data.

RESULTS AND CONCLUSIONS

Batch Test And Field Tracer Test Results

Table 1 contains rock analysis and batch test results for all samples shown on figure 1. All batch tests were performed with the technique described above.

All highwall samples are found to be free of, or have very low levels of carbonate material. This includes the highly weathered joint-fill material collected from the Middle Kittanning highwall. H-1 and H-1w are the only highwall samples which have a high potential acidity as calculated from their sulfur content. With the exception of the sulfur-rich samples, the batch test results indicate each of the highwall samples to possess a significant capacity for consuming acidity.

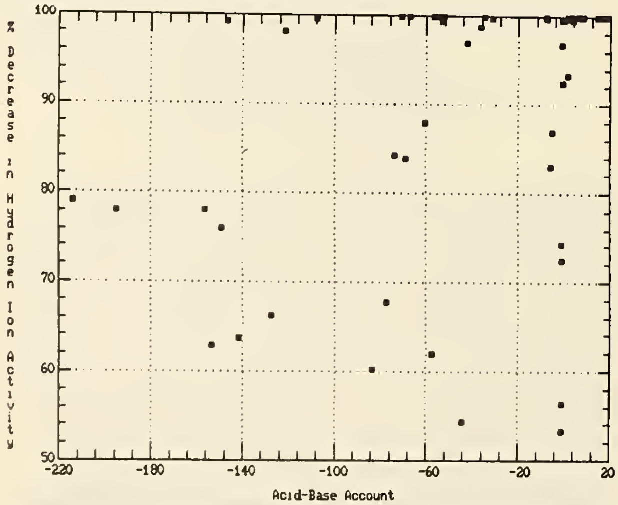


Figure 9.--Decrease in H^+ activity versus acid-base account (all samples, account in tons of $CaCO_3$ equivalent per thousand tons of material).

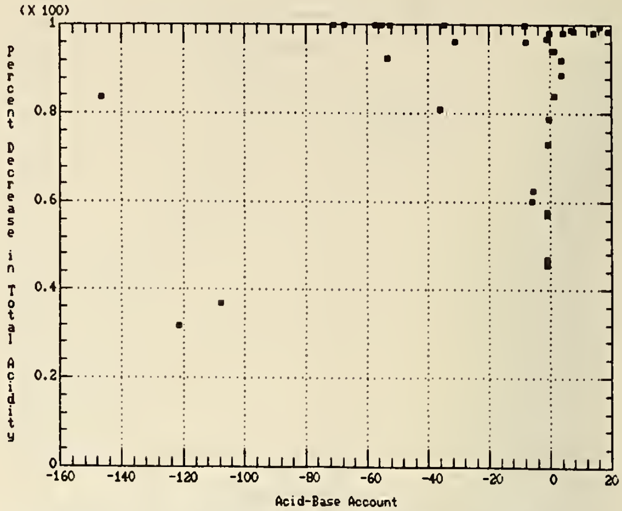


Figure 10.--Percent decrease in total acidity versus acid-base account of samples which consumed acidity (y-axis in hundreds of percentage points).

Figure 9 is a scatter plot of the percent decrease in hydrogen-ion activity versus rock sample acid-base account. All batch tests performed resulted in a decrease of hydrogen-ion activity, including batch tests where total acidity increased and the acid-base account was strongly negative. This adds more support for considering this a measurement of the hydrogen-ion distribution coefficient.

Figure 10 is a scatter plot of percent decrease in total acidity versus acid-base account. The only data presented on this figure are the results of batch tests where total acidity decreased. Acidity was consumed by all samples having an acid-base account greater than -40 tons $CaCO_3$ equivalent per thousand tons of material.

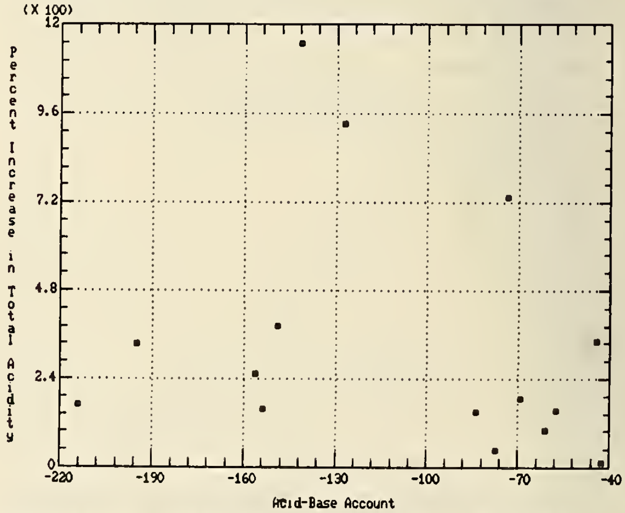


Figure 11.--Percent increase in acidity versus acid-base account of samples which produced acidity (y-axis in hundreds of percentage points).

Table 1.-- Rock Sample characteristics and batch test results.

Sample	Carbonate Carbon (%)	Neutralization Potential	Maximum Potential Acidity	Acid-Base Account	Percent Decrease of Hydrogen Ion Activity	Percent Decrease of Total Acidity	Percent Decrease of Specific Conductance
		(tons CaCO3 equivalent per thousand tons of material)					
H-1	0.000	0.0	150	-150	63	-160	-15
H-2	0.000	.0	5.7	-5.7	83	60	42
H-3	0.000	1.5	2.1	-0.6	92	79	63
H-4	0.000	0.0	1.1	-1.1	73	57	52
H-5	0.000	0.0	1.0	-1.0	53	46	38
H-6	0.001	2.2	1.1	1.2	93	84	66
H-1w	0.000	0.0	84	-84	60	-150	-5.1
H-2w	0.000	0.0	5.5	-5.5	87	63	30
H-3w	0.000	2.2	3.2	-0.9	97	73	68
H-4w	0.000	0.0	1.0	-1.0	74	58	56
H-5w	0.000	.0	1.0	-1.0	56	47	43
H-J1	0.011	4.0	4.3	-0.3	99	98	69
H-Jd	0.017	5.2	6.2	-1.0	99	97	72
A-1	0.486	8.7	4.3	4.4	99	98	65
A-2	0.000	0.0	140	-140	64	-1200	-110
A-3	0.113	0.0	74	-74	84	-730	-89
A-4	0.444	10	18	-8.0	99	96	60
B-1	0.277	5.2	4.0	1.2	100	94	61
B-2	0.264	0.0	43	-43	97	-15	0.5
B-3	0.002	0.0	200	-200	78	-340	-26
B-4	0.551	6.0	42	-36	99	81	47
C-1	0.293	6.9	3.3	3.7	99	92	62
C-2	0.653	11	10	1.0	99	94	51
C-3	0.249	0.0	160	-160	78	-260	-18
C-4	0.513	5.7	59	-53	99	92	57
D-1	0.460	10	3.4	6.6	100	99	63
D-2	0.514	16	25	-9.0	100	100	69
D-3	0.058	0.0	130	-130	66	-940	-98
E-1	0.598	18	3.3	15	100	98	64
E-2	0.442	6.9	130	-123	98	32	35
E-3	0.469	7.9	150	-142	99	84	54
E-4	0.774	20	12	8.0	100	98	64
F-1	0.920	24	4.5	20	100	99	61
F-2	0.715	21	82	-61	88	-99	-29
F-3	0.517	5.2	74	-69	84	-190	-42
F-4	0.524	5.4	37	-32	99	96	48
Co-1	0.724	8.8	5.2	3.6	99	89	70
Co-2	0.000	0.0	44	-44	54	-340	-22
Co-3	0.000	0.0	58	-58	62	-150	-0.1
Co-4	0.000	0.0	77	-77	68	-48	20
Co-5	1.274	91	75	16	100	100	46
Co-6	0.609	42	77	-35	100	100	39
Co-7	0.338	31	83	-52	100	100	28
Co-8	0.309	31	88	-57	100	100	33
Co-9	0.473	42	97	-55	100	100	41
Co-10	0.287	27	98	-71	100	100	45
Co-11	0.333	32	99	-67	100	100	30
Co-12	0.127	11	120	-109	99	37	-1.6
Co-13	0.001	0.0	150	-150	76	-390	-38
Co-14	0.002	0.0	210	-210	79	-170	-6.3

Figure 11 is a scatter plot of percent increase in total acidity versus acid-base account. The only data presented on this figure are the results of batch tests where total acidity increased. A comparison of this figure to figure 10 shows that some batch tests of samples with acid-base accounts greater than -140 and less than -40 resulted in a decrease in total acidity while others resulted in an increase in total acidity. Analysis of rock parameters not listed in table 1 did not clearly show which characteristics indicate whether a sample will increase or decrease acidity in the laboratory batch experiments. Further research is needed in this area.

Figure 12 shows the acid-base accounting for all of the drill-cutting samples. Fifteen of the 23 samples are found to have a negative account. The average acid-base account of the 23 samples is -53 tons $CaCO_3$ equivalent per thousand tons of material. Figure 13 shows the percent change in total acidity for each drill-cutting sample. Positive numbers indicate percent decrease of the initial total acidity. Negative numbers indicate percent increase of the initial total acidity. Fifteen of the 23 samples consumed acidity. As mentioned earlier, each test resulted in a decreased hydrogen-ion activity. Field acid-injection tracer tests were conducted

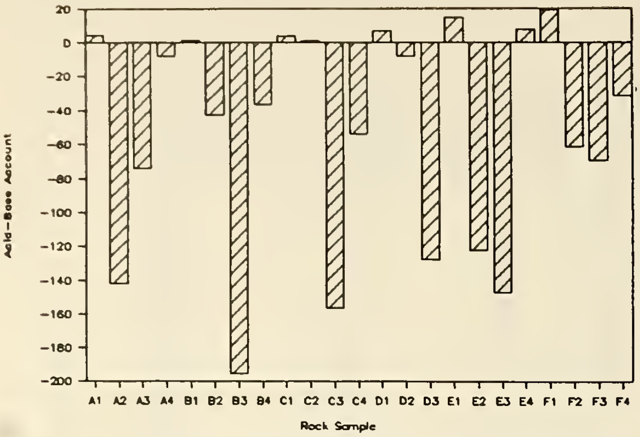


Figure 12.--Acid-base account of drill cutting samples (in tons of $CaCO_3$ per thousand tons of material).

in the drillholes from which these samples were collected. The tests resulted in an approximate 50% decrease in both the hydrogen-ion activity and total acidity. These calculations consider the natural dispersion of the aquifer. Although the aquifer rock was found to have a negative acid-base account, and some drill-cutting batch tests resulted in significant acid production, these field tests suggest that the natural abatement processes dominate in an acid-contaminated aquifer. If pyrite oxidation does occur, it is of secondary importance in acid migration predictions. A detailed description of the field methods and the results is not presented here, but will be published in the future.

Summary Statements

(1) A laboratory technique has been established which may enable the quantification of the hydrogen-ion distribution coefficient. With additional research, it may eventually provide the necessary information for modeling acid contaminant transport.

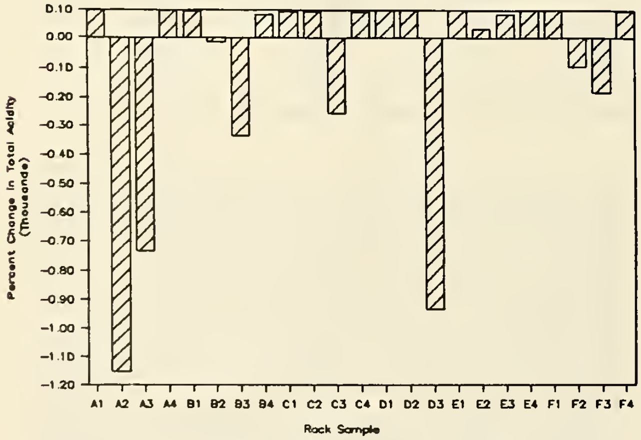


Figure 13.--Percent change in total acidity for drill-cutting samples (y-axis in thousand of percentage points. Positive no. indicates acidity consumed, negative no. indicates acidity produced).

(2) All laboratory batch tests resulted in an increase in pH, regardless of whether acidity was consumed or produced and regardless of the acid-base account.

(3) All samples lacking carbonate material and having low sulfur content were found to have a significant acid-consuming capacity.

(4) All samples having an acid-base account greater than -40 (tons $CaCO_3$ equivalent per thousand tons of material) consumed acidity in the batch experiments.

(5) Some samples having an acid-base account greater than -140 but less than -40 consumed acidity in the batch experiments.

(6) Field tracer tests show that an aquifer can have a significant natural capacity to abate acid mine drainage even if it has an overall negative acid-base account and contains some rock which will produce acidity in laboratory batch experiments.

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PREDICTION OF ACID MINE DRAINAGE FROM DULUTH COMPLEX MINING WASTES IN NORTHEASTERN MINNESOTA[1]

Kim Lapakko[2]

Abstract. Ten Duluth Complex drill core samples, with sulfur contents ranging from 0.47 to 2.17 percent, were leached in a laboratory experiment. The variation in sulfur content was due largely to fluctuations in iron sulfide content. Solids containing 0.8 percent sulfur or less produced neutral drainage while, with one exception, solids with sulfur contents of 0.92 percent or more produced acidic drainage. The results indicated that acid production due to oxidation of sulfide minerals containing iron, such as pyrrhotite, increased linearly as the sulfur content increased. The acid consumption due to silicate mineral dissolution was relatively constant despite minor variations in the silicate mineralogy. A sample containing 1.17 percent sulfur produced neutral drainage due to the buffering provided by a calcium carbonate content of three percent. Leaching of a sample from a test stockpile indicated that the fine fraction of stockpile solids exerted a major influence on the drainage chemistry. The pH range and temporal variation of drainage from solids containing 0.92 percent sulfur was similar to that from a test stockpile with a bulk sulfur content of 0.6 percent. Analysis of the test stockpile solids indicated that particles smaller than 2.0 mm in diameter comprised about 12 percent of the stockpile mass and had a sulfur content of 1 percent. The laboratory results suggest these small particles exert a major influence on stockpile drainage quality, most likely due to their elevated sulfur content and specific surface area.

INTRODUCTION

The Duluth Complex, located in northeastern Minnesota, is an intrusive formation containing low-grade copper and nickel sulfides (Listerud and Meineke 1977). These deposits comprise 25 percent of the United States' copper resource and the nation's largest nickel sulfide resource (Minnesota Environmental Quality Board 1980, Kingston et al. 1970). Development of these resources would require open pits which will eventually fill and discharge water, possibly containing elevated concentrations of trace metals, to the environment (Thingvold et al. 1979).

Based on conceptual models, the open pits could produce an estimated 4 to 10 km^2 of waste rock stockpiles (Sturgess 1981; Veith 1978), which would generate an estimated runoff of 1.5 to 3.8 billion liters in a year of average precipitation (Hewett 1980). Trace metal concentrations in runoff from waste rock stockpiles at the Erie Mining Company Dunka Mine were 10 to 10,000 times natural background levels of streams in the area (Eger et al. 1981). Since these metals have been shown to be toxic at low aqueous concentrations (United States Environmental Protection Agency 1976), means of mitigating the impacts of mining drainage will be required for these resources to be developed.

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The degree of mitigation required may be a function of the potential for trace metal and acid release from a given stockpile. This potential is dependent upon, among other factors, the composition of the stockpiled rock. Examining dissolution with respect to all chemical and mineralogical variables would, at best, be extremely complicated. Characterizing mine wastes with respect to these variables in the course of operations is also impractical. Consequently, a more simplistic course of experimentation, using sulfur content as the independent variable, was adopted.

The effect of sulfur content on the leaching of Duluth Complex mining wastes has been examined for a limited number of samples. Field tests were conducted on test stockpiles constructed of rock removed from a test shaft. Over a 6-year period, test stockpiles containing 0.8 and 1.4 percent sulfur produced acid leachate while piles containing 0.6 percent sulfur did not (Eger and Lapakko 1985). Subsequent data indicate the drainage pH has at times decreased below pH 5 at one of the four piles containing 0.6 percent sulfur. In shake flask tests, neutral leachate was generated by tailings containing 0.92 percent sulfur or less, while acidic leachate was generated by tailings with sulfur contents equaling or exceeding 2.65 percent (Natarajan and Iwasaki 1983).

The rate of metal sulfide oxidation has been reported to be directly proportional to the reactive sulfide mineral surface area available (Lapakko 1980; Nelson 1978; Sato 1960a, 1960b; Sato and Mooney 1960). In turn, the available surface area of nonporous solids is a function of the sulfide content of the rock, particle size, and the roughness of the surface. Since the copper and nickel content of mine wastes is small, the sulfur content is an indicator of iron sulfide minerals, which are of major importance due to their role in acid production.

Since other sulfides are present in limited quantities, their influence is diminished and to some extent uniform. By using uniformly small solids, the influence of particle size and host rock association of the iron sulfides is normalized. If the sulfides are liberated in small size fractions, the sulfur content will represent the available sulfide surface area, assuming specific surface area does not vary greatly among sulfide minerals of the same particle size. Since all the sulfide surface area is known to be available, acid production rates per unit sulfide surface area can be determined. Using this normalized value, the acid production rate can be extrapolated to mining wastes based on their available sulfide surface area. This extrapolation will allow appropriate mitigation based on the rock composition.

The use of sulfur content as the independent variable neglects the effects of many other variables, environmental as well as compositional, on the leaching of mine wastes. Although there is a given degree of compositional uniformity within an ore body, there are deviations from the norm. To accurately assess the leaching potential of mining wastes from a given body, a large number of samples must be analyzed. This implies the use of efficient and accurate laboratory techniques from which results can be extrapolated to operational conditions. This study involved examination of the leaching behavior of a small number of Duluth Complex samples with variable sulfur contents, and determination of the feasibility of extrapolating laboratory results to operational conditions.

METHODS

Materials

An experiment was conducted to examine the effect of solid phase sulfur content on the quality of drainage from Duluth Complex mining wastes. The sulfur content of the 11 samples examined ranged from 0.47 to 2.17 percent. Acid digestion (U.S. Bureau of Mines 1980) and subsequent analysis revealed typical solid phase copper and nickel contents of 0.13 to 0.23 and 0.05 to 0.09 percent, respectively (table 1). The samples were selected to approximate mining wastes, based on a 0.2 percent copper cutoff. Mine waste would, of course, be larger with a maximum diameter of approximately 45 cm for under-ground mines and 120 cm for open pits. Plagioclase, olivine, pyroxenes, and biotite were the predominant minerals, as determined by examination of polished thin sections with an optical microscope (table 2). Specific surface area was determined by single point BET nitrogen adsorption by A. U. Baes of the Soil Science Department at the University of Minnesota, St. Paul.

With one exception, the solids were MINNAMAX core samples which had been drilled from 1974 to 1977. The core samples had been crushed to minus 1/4 inch, placed into plastic bags, and stored inside 55-gal barrels at the MINNAMAX site near Babbitt, MN. Under the direction of Karl Smith, the samples were processed for experimental use at the Mineral Resource Research Center at the University of Minnesota. The plus 10-mesh fraction was selected for experimentation in order to minimize the amount of surface area exposed to oxidation while the samples had been stored after drilling. This fraction was stage crushed using a pulverizer and wet-screened to segregate the -100/+270 mesh fraction for use in laboratory tests.

The remaining sample (1.26 pct S) was collected from a test stockpile which was constructed in April 1977 at the MINNAMAX

Table 1.--Elemental composition of 11 Duluth Complex samples, values in weight percent.

S	Cu	Ni	Co	Zn	S with FeS[1]	Fe	Ca	Mg	Na	K	Pct of total S bound by Fe
0.47	0.23	0.060	0.011	0.017	0.31	15.2	7.8	7.9	2.6	0.37	65
.59	.13	.072	.013	.0070	.44	11.5	11	7.1	3.1	.27	75
.80	.19	.067	.011	.010	.66	13.7	9.8	6.6	3.0	.42	82
.92	.091	.049	.014	.016	.83	24.6	8.0	11.8	2.2	.42	90
1.17	.23	.082	.011	.015	1.0	16.3	14.6	10.5	1.4	.42	85
1.24	.19	.066	.012	.013	1.1	15.4	6.8	10.1	2.3	.42	91
1.35	.23	.086	.018	.011	1.2	18.4	9.4	7.3	2.4	.30	87
1.87	.17	.088	.021	.011	1.7	19	9.6	8.7	7.5	.86	92
2.01	.20	.055	.012	.020	1.9	19.6	5.3	5.1	2.2	1.10	93
2.17	.20	.078	.010	.027	2.0	8.5	1.7	2.9	2.6	1.83	93
1.26[2]	.55	.20	.018	.014	.97	18	8.0	8.0	2.7	.44	77

[1] Calculated as the sulfur not bound by Cu, Ni, Co, or Zn assuming all trace metals were bound by sulfur in a 1:1 mole ratio of sulfur to metal.

[2] Sample from test pile.

Table 2.--Approximate modal compositions of Duluth Complex Samples.
(By Tatiana Sabelin, Mineral Resources Research Center, University of Minnesota).

Mineralogy (%)

PCT S	Olivine	Pyroxene	Plagioclase	Biotite	Opaque	Amphibole	Other	Calcite
0.47	30	10	45	5	8	-	2	-
.59	17	4	68	2	5	-	4	-
.80	20	8	59	4	7	-	2	-
.92	31	27	24	2	16	-	-	-
1.17	19	15	28	2	8	-	25	3
1.24	17	27	47	1	5	-	3	-
1.35	10	14	57	-	9	-	10	-
1.87	18	4	57	2	10	-	9	-
2.01	7	15	59	6	13	-	-	-
2.17	15	8	51[1]	6	17	-	3	-
1.26[2]	15	11	49	3	16	2	4	-

[1] Includes plagioclase and quartz; of this total maybe as much as 1/3 to 1/2 is quartz.

[2] Sample from test pile.

site. The pile was constructed of rock mined during the development of a test shaft. When part of the test pile was removed in September 1982 a representative sample, weighing over 3 tons, was collected for analysis of particle size distribution, specific surface area, chemistry, and mineralogy (Lapakko et al. 1986). A subsample of stockpile material in the -100/+270 mesh fraction was collected for use in the experiments.

Leaching Procedure

Several techniques have been used in laboratory leaching of mining wastes (Caruccio 1986; Ferguson and Mehling 1986). The method used was based on the principle that sulfide minerals oxidize in the presence of atmospheric oxygen and water (Gottschalk and Buehler 1912; Caruccio et al. 1980). Samples (75 g) of -100/+270 mesh rock were placed into the upper segment, or reactor, of a two-stage filter unit and rinsed with 200-mL volumes of distilled deionized water. Seven of the solids were run in duplicate while single reactors were used for the remaining four solids (0.47, 0.59, 1.35, and 2.01 pct S). The rinse water was allowed to remain in contact with the solids for five minutes and filtered through a 0.45 micrometer filter. Between rinses the solids were kept in the upper segment and stored in a box to dry. A cover was placed about 3 cm above the upper edge of the box to allow drying of the solids and prohibit the input of airborn debris. A thermostatically controlled heating pad was placed beneath the box to maintain a constant temperature. Water containers were placed in the box in an attempt to maintain a fairly constant humidity. Temperature and relative humidity in the box were monitored four to five times per week. The average temperature was 25°C with a standard deviation of 1.0°C, while the corresponding values for relative humidity were 56 and 9.1 percent.

At the beginning of the experiment, the solids were rinsed five times to remove oxidation products generated after crushing and wet sieving. After this initial washing the solids were rinsed weekly. Four rinses were used after one week and three rinses after two weeks. Two rinses were found to remove the majority of sulfate from the solids and were used in subsequent weeks.

The rinse water, or drainage, was analyzed for specific conductance, pH, sulfate, copper, nickel, cobalt, zinc, calcium, magnesium, sodium, and potassium. Specific conductance was analyzed using a Myron L conductivity meter, while a Radiometer 29 pH meter was used for pH analyses. Sulfate was analyzed using either the barium sulfate turbidimetric technique (APHA et al. 1975) or a Technicon autoanalyzer. Metals were analyzed with a Perkin Elmer 603 atomic absorption spectrophotometer. The experiments were conducted at the site previously leased by MINNAMAX, which is presently leased by Kennecott Minerals (fig. 1).

RESULTS AND DISCUSSION

Laboratory Data

Drainage pH generally decreased as the solid phase sulfur content increased and as the duration of leaching increased. The pH of drainage from solids containing less than 0.9 percent S was consistently above 6, while drainage from solids containing more than 1.3 percent S was typically below pH 6. Between 0.9 and 1.3 percent S was a transition zone. Drainage pH from one of the three transitional solids continuously remained above 7.5 (fig. 2). The drainage pH from the other two transitional solids was initially in the neutral range, but steadily decreased to about 4.2 where it plateaued. The tendency for drainage pH to decrease and level over time was observed with most solids, but the decrease was most pronounced with these transitional solids. These pH trends were the net result of acid production by the oxidation of iron sulfide minerals and acid consumption by the dissolution of silicate minerals.

The dissolution of iron sulfide minerals leads to the production of acid, as indicated by reaction 1 (Nelson 1978).

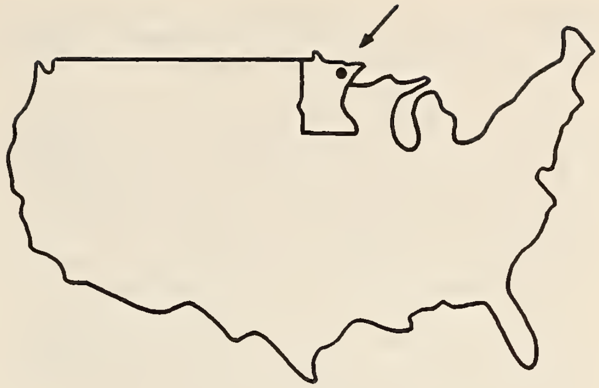

Figure 1.--Project site in northeastern Minnesota.

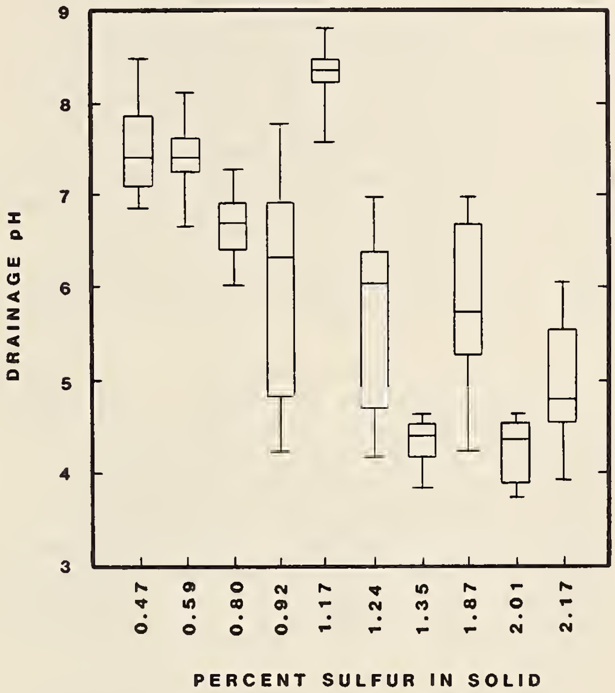

Figure 2.--Drainage pH versus sulfur content of the solid phase. Horizonal lines represent 25, 50 and 75 per percentiles, as well as the minimum and maximum values during the entire experiment.

The iron sulfide oxidation may be

$$FeS(s) + (3/2)H_2O + (9/4)O_2 = FeOOH(s) + 2H^+(aq) + SO_4^{2-}(aq) \quad (1)$$

influenced by microbial activity (Natarajan et al. 1982) and galvanic interactions with other sulfide minerals (Natarajan and Iwasaki 1983), as well as other factors. The oxidation of sulfide to the hexavalent sulfur in sulfate does not contribute acid. The two moles of acid produced are the net result of the oxidation of ferrous iron and the subsequent precipitation of ferric iron, as lepidocrocite for example (Nelson 1978; Sung and Morgan 1980).

The rate of iron sulfide oxidation was reflected by the appearance of sulfate in solution. In an oxidizing environment, sulfate is the ultimate reaction product of sulfide oxidation. Over the aqueous concentration range observed in the laboratory samples, sulfate will remain in solution as opposed to precipitating.

The hypotheses that sulfate was the dominant oxidation product and was stable in solution were supported by the fact that sulfate concentrations in stored samples were constant over several months. If reduced sulfur species were present they would have oxidized over this period and increased the sulfate concentration. Similarly there was no decrease in sulfate concentration which would result if sulfate precipitated from solution. The fact that more than 90 percent of sulfate concentrations were less than 50 mg/L, with none exceeding 130 mg/L, further indicates that sulfate precipitation or adsorption was unlikely. Some sulfate, or other sulfide oxidation products, may have been adsorbed onto the solids in the reactor. However, the multiple rinses indicated that little sulfate was removed from the solids by distilled water after the two rinses.

Since sulfide was oxidized to sulfate and aqueous sulfate was stable, the rate of sulfide oxidation equals the rate of appearance of sulfate in solution at steady state. Since 82 to 93 percent of the sulfide present in these samples was bound by iron (table 1), oxidation of these iron sulfides was most likely the major sulfate source. Pyrrhotite is the predominant iron sulfide in the Duluth Complex (Bonnichsen 1972), and in these samples.

The rate of sulfate appearance was proportional to the mean sulfate concentration, since the rinse volumes were essentially equal, the mass of solids leached was constant at 75 g, and the rinse interval was constant. Mean concentrations from weeks 6 through 17 were used since a) sulfate concentrations during the initial 5 weeks were typically low and not representative of the sulfate release in general, and b) after the initial 17 weeks, the rinsing interval for some of the solids was extended beyond the standard duration of 1 week, which affected the rate of sulfate release. The weekly sulfate concentrations were fairly constant over this period, suggesting the oxidation of sulfide to sulfate had approached steady state. However, some of the solids subsequently generated sulfate concentrations which fluctuated from this narrow range. Although a steady-state condition may not have been reached for all solids, the sulfate data provide the best approximation of the sulfide oxidation rate during the initial stage of experimentation. The phrase "initial apparent steady-state period" best describes this phase.

The rate of sulfide oxidation, as reflected by mean sulfate concentrations, correlated highly with the solid phase sulfur content. The percent sulfur in the solid phase accounted for 77.6 percent of the variation in the sulfide oxidation rate (r = 0.776). The r value increased to 0.963 when two outlying data points at 1.35 and 1.87 percent S were ignored.

The degree of correlation for the entire data set increased when variations in specific surface area among the solids were taken into account. The anomalous sulfate concentrations, from the solids containing 1.35 and 1.87 percent S, were higher than predicted by the linear model describing the eight remaining points (fig. 3). Although all solids were in the -100/+270 mesh size fraction, limiting particle diameter to the range of 0.053 to 0.149 mm, there were minor variations in specific surface area. The specific surface areas, as determined by BET nitrogen adsorption, of the two anomalous solids were 65 to 80 percent higher than the average of the remaining solids. To account for this variation, the available sulfide surface area per gram solid was estimated as the product of the sulfur content and the specific surface area. The correlation coefficient was 0.846 for the linear variation of sulfate release rate with respect to this available sulfide surface area. This dependence is consistent with a surface reaction dominating the sulfide oxidation.

The r value increased to 0.962 when the data for the solid containing 1.17 percent sulfur was omitted. Sulfate release from this solid was lower than predicted by the linear model describing the remaining nine data points. This was the only sample containing calcium carbonate, which may have been responsible for the elevated surface area of this sample. The elevated pH of the drainage from this sample may also have inhibited the rate of sulfide oxidation (Nelson 1978).

Some of the acid generated was consumed, or neutralized, by the dissolution of silicate minerals. Plagioclase, olivine, and pyroxenes are the silicate minerals which comprise the majority of the host rock. The dissolution of anorthite, which is a member of the plagioclase solution series, is represented by the following reaction (Stumm and Morgan 1981).

$$\begin{aligned}&CaAl_2Si_2O_8(s) + 2H^+(aq) + H_2O = \\ &Ca^{2+}(aq) + Al_2Si_2O_5(OH)_4(s) \qquad (2)\end{aligned}$$

The dissolution of these minerals in laboratory experiments has often been reported as parabolic with respect to time. Initially the hydrogen ions in solution are

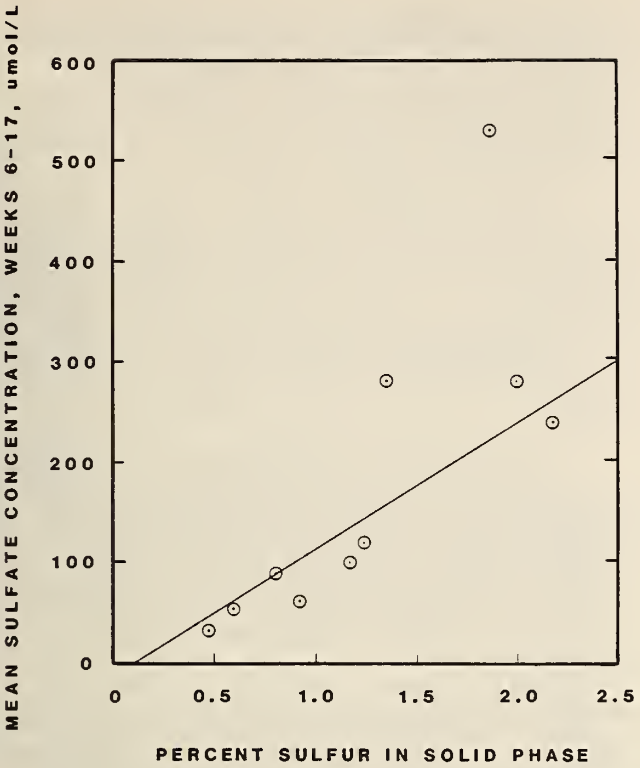

Figure 3.--Sulfide oxidation rate, as represented by mean sulfate concentration, versus percent sulfur. Points at 1.35 and 1.87 percent S were excluded from the regression analysis which determined line shown.

rapidly and reversibly exchanged with alkalai ions on the mineral surface (Holdren and Berner 1979, Busenberg and Clemency 1976). The rate of release subsequently decreases, eventually becoming linear with respect to time (White and Classen 1979, Busenberg and Clemency 1976). The rate of dissolution during this phase is relatively slow (Siegel 1981, White and Classen 1979, Busenberg and Clemency 1976).

Dissolution of the silicate minerals was rapid enough to neutralize the acid generated by iron sulfide oxidation in the solids containing 0.8 percent S or less. The pH of drainage from these solids remained above 6. For the solids containing at least 1.35 percent S, reflecting the higher content of iron sulfides, the acid production rapidly overwhelmed the buffering capacity. The drainage from the solids containing 0.92 and 1.24 percent S was initially neutral but gradually decreased, indicating that the rate of iron sulfide oxidation ultimately exceeded the dissolution rate of the silicate minerals present.

The balance of acid production by iron sulfide oxidation and acid consumption by silicate mineral dissolution is illustrated semiquantitatively by comparing sulfate concentrations with the sum of calcium and magnesium values. The release of one mole of sulfate represents the production of two moles of acid, while the release of one mole of calcium or magnesium represents the consumption of two moles of acid (reactions 1 and 2, respectively). Initially the sum of calcium and magnesium concentrations exceeded the sulfate concentration, thus the ratio of the sum to sulfate was greater than one. This indicates that the rate of acid consumption by silicate mineral dissolution initially exceeded the rate of acid production by iron sulfide oxidation. This is borne out by the fact that the drainage pH was initially in the neutral range (fig. 4).

The rate of acid production gradually increased over the first 18 weeks, but the rate of acid consumption increased concomitantly and neutralized the acid produced. After 20 weeks the acid production increased dramatically and the silicate mineral buffering was overcome. At this time, the ratio of the sum of calcium and magnesium concentrations to sulfate concentration dropped below a value of one and pH decreased, ultimately reaching 4.5.

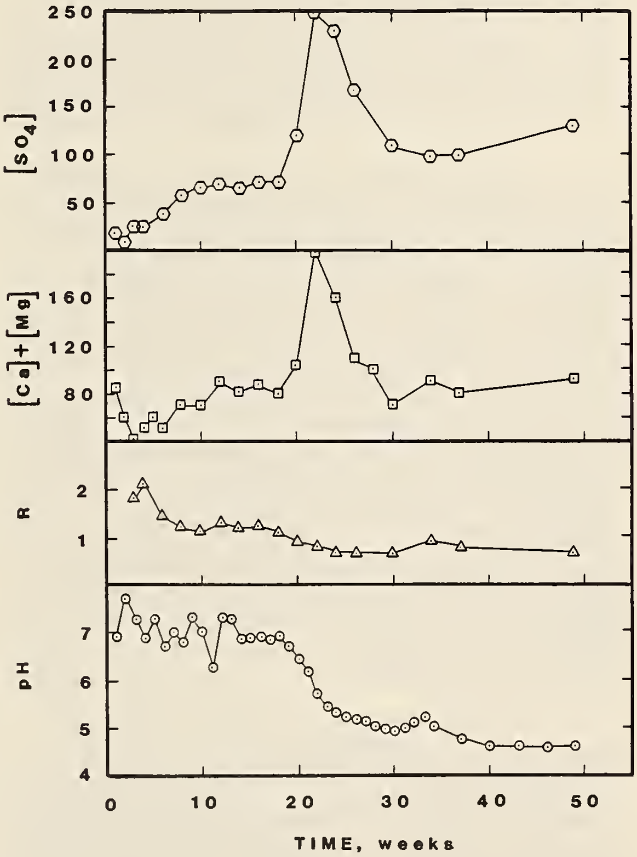

Figure 4.--Drainage from 0.92 percent S solids versus time. Concentrations are in micromoles per liter, and R is the ratio of the sum of Ca and Mg concentrations to the sulfate concentration.

The buffering supplied by the silicate minerals was fairly uniform among the solids, despite differences in silicate mineralogy (table 2). Apparently these differences had little effect on the overall rate of silicate mineral dissolution. The sample containing 1.87 percent S did exhibit slightly greater buffering and calcium release, and its composition is being examined in greater detail.

The uniformity in buffering among the silicate minerals is particularly important in predicting drainage pH. The primary copper-nickel mineralization of the Duluth Complex occurs as disseminated sulfides in a troctolitic-gabbroic series of rocks which intrudes an anorthositic and felsic series of older rocks (Weiblen and Morey 1975). About 90 percent of the host rock is composed of silicate minerals, predominantly plagioclase, olivine, and pyroxenes (Stevenson et al. 1979). If the buffering supplied by these minerals is somewhat uniform, the drainage pH will be controlled by the rate of acid generation due to oxidation of iron sulfides. Pyrrhotite is the predominant form of these iron sulfides (Bonnichsen 1972). Determination of the oxidation rate based on sulfur content will allow prediction of the acid-producing potential of mining wastes based on their sulfur content. Investigation of a wider variety of rocks will lend further insight into the influence of the various silicate minerals on buffering, as well as other factors.

In contrast to the general uniformity in buffering, the solid containing 1.17 percent S, despite exceeding the sulfur content of one of the acid solids, produced drainage pH values which were typically above pH 8. Mineralogical analysis of this solid indicated a calcium carbonate content of about 3 percent. Dissolution of this calcium carbonate was reflected by calcium concentrations in drainage from this solid which were three to five times those in drainage from all but one other solid. Due to its rapid dissolution, the small amount of calcium carbonate was able to provide more buffering than the silicate minerals, which typically comprised more than 80 percent of the solids. This further emphasizes the slow kinetics of, and limited buffering by, dissolution of the silicate minerals.

The effectiveness of the silicate mineral buffering may have been further limited by the physical factors in the reaction environment. Iron sulfides can be oxidized by the oxygen and water vapor present in the air, while silicate dissolution due to the presence of oxygen and water vapor is negligible. The acid resulting from iron sulfide oxidation may contact only the silicate minerals in the immediate vicinity of the iron sulfides. Dissolution of these silicates can leave a less reactive solid phase such as kaolinite (reaction 2; Busenberg 1978), which may further inhibit the transport of acid to other mineral surfaces and further limit buffering. This inhibition of buffering reactions may contribute to the increased metal recovery associated with the "resting" of leach columns and dumps in metallurgical work.

In a submerged reaction environment, such as that in batch reactors, the acid generated could be readily transported to silicate mineral surfaces via the aqueous medium. As a result, batch reactor data may overestimate the buffering available in an environment subject to wet-dry cycling, such as stockpiles and unsubmerged mine walls.

As drainage pH decreased, trace metal release increased, and this increase was quantified by linear regression analysis of the base 10 logarithm of metal concentration versus pH. For the log copper concentration versus pH plot, the slope was -1.11 ($r=-0.944$, $n=38$), and the corresponding slope for nickel was -0.99 ($r=-0.902$, $n=40$). Similar trends were observed for cobalt and zinc. This increase in trace metal concentrations further magnifies the problems of acid drainage. The slopes indicate that as pH decreases one unit, copper and nickel concentrations will increase by about an order of magnitude.

Comparison of Laboratory and Field Data

Laboratory data on the test stockpile solids suggested that the smaller particles had a marked influence on the stockpile drainage quality. Particles smaller than 2.0 mm in diameter comprised about 12 percent of the total stockpile mass. The weighted average sulfur content of these particles was 1.0 percent as compared with 0.6 percent S for the bulk rock. The sulfur content of these particles tended to increase as particle size decreased, with particles of diameter less than 0.053 mm having a sulfur content of 1.86 percent (Lapakko et al. 1986).

The pH range generated in the laboratory was quite close to that observed for the test stockpile drainage in 1982, when the solids were collected (fig. 5). Comparison with field data from subsequent years is somewhat tenuous since the stockpile was dismantled, and the rock was divided among six different test plots. The diameter of the particles used in the laboratory tests was in the range of 0.053 to 0.147 mm, and particles in this size range comprised only about 3 percent of the stockpile mass. The sulfur content of the particles was 1.26 percent, as compared with 0.6 percent for the bulk rock. The laboratory pH was slightly lower than that observed in the field. This suggests that the particle size range dominating the stockpile drainage chemistry may be slightly larger than that used in

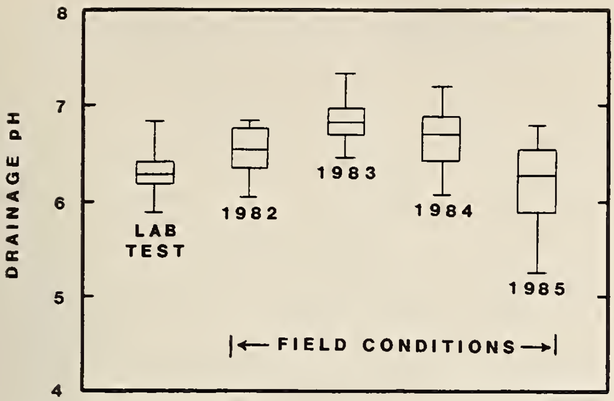

Figure 5.--Drainage pH in laboratory compared to field values. Note: In September 1982 the test pile from which these laboratory solids were taken was dismantled and placed into test plots. Field data subsequent to 1982 are from these plots.

the laboratory, assuming similar sulfide oxidation rates in the two settings. The field rates may have differed from laboratory rates due to fluctuations in ambient temperature and humidity, or inhibited by restricted oxygen transport. If so, another size range may have been the dominant influence on the stockpile drainage chemistry. Nonetheless, drainage pH from the 0.053 to 0.147 mm particles in the laboratory was quite close to that from the test stockpile in the field.

Particle size is important for several reasons. As previously mentioned, sulfur content increased as particle size decreased. Sulfide minerals are softer than the silicate minerals and, therefore, are more prone to breakdown. Consequently, they tend to concentrate in the smaller size fractions. Secondly, the surface area of the fines is relatively high since specific surface area increases as particle size decreases. Since the rate of iron sulfide oxidation was proportional to the available surface area, the rate of sulfide oxidation per unit mass of these particles is magnified.

Thirdly, sulfide minerals in the small size fractions are most likely to be free rather than occurring as interstitial or included minerals. For Duluth Complex samples, the diameter at which sulfides are liberated from the host rock has been estimated as 0.074 mm (Weiblen and Morey 1976); mineral beneficiation studies suggest a value of about 0.2 mm (Vifian and Iwasaki 1968). In particles larger than this critical size, a large fraction of the total sulfide surface area would be protected by the host rock, and therefore unavailable for reaction. Leaching tests run with larger particles tended to yield lower rates of sulfide oxidation and acid production. For example, the leaching of minus 10 mesh (diameter less than 2 mm) tailings containing 0.92 percent S produced neutral leachate (Natarajan and Iwasaki 1983), while 0.053-mm to 0.147-mm solids of the same sulfur content produced acidic drainage in the present study. As discussed earlier, the submerged reaction environment in the shake flask leaching of tailings may also have increased buffering efficiency by permitting acid contact with a larger silicate surface area.

The pH of drainage from test stockpiles also decreased as the sulfur content increased. The most recent annual median pH values from piles containing 0.6 percent S were in the range of 5.25 to 6.5. The corresponding pH values for stockpiles with sulfur contents of 0.8 and 1.4 percent were about 4.25 and 3.6, respectively. These values suggest that stockpiles containing 0.6 percent S are near the boundary of acid production. In the laboratory this boundary occurred between 0.80 and 0.92 percent S. This indicates that the laboratory tests simulate the leaching behavior of stockpiled solids having a bulk sulfur content roughly 68 to 79 percent of the laboratory solids. This "effective sulfur content" of stockpiled rock will, however, vary depending on the particle size distribution of the stockpiled solids. Additional study on the effects of both composition and particle size on drainage quality are required in order to more accurately extrapolate laboratory results to stockpiles in the field.

The laboratory data also closely simulated other aspects of stockpile drainage chemistry, indicating that the two reaction regimes were similar. The variation of pH over time was similar in both cases. The drainage pH in the field tended to decrease over time, reflecting the decrease in buffering by silicate mineral dissolution. For the stockpiles containing 0.6 percent S the pH decrease over time was gradual, but for the higher sulfur piles the decrease was relatively rapid (fig. 6). After the initial pH decrease, the drainage pH from the high sulfur piles was fairly stable. In the laboratory tests, a rapid pH decrease and subsequent period of relatively stable pH was also observed for samples with relatively high sulfur contents. The ratio of the sum of calcium and magnesium release to sulfate release traced pH fluctuations in the field as in the laboratory.

Metals concentrations increased as pH decreased in both laboratory and field settings. The slopes for the log metal versus pH relationships, however, were steeper in the laboratory than in the field. As previously mentioned, the laboratory data for the 0.92 percent solids indicated slopes of -1.11 for copper and -0.99 for nickel. Using the annual median values for metal concentration and pH for all stockpile drainages, the slopes for copper and nickel were -0.76 and -0.66, respectively (Eger and Lapakko 1985).

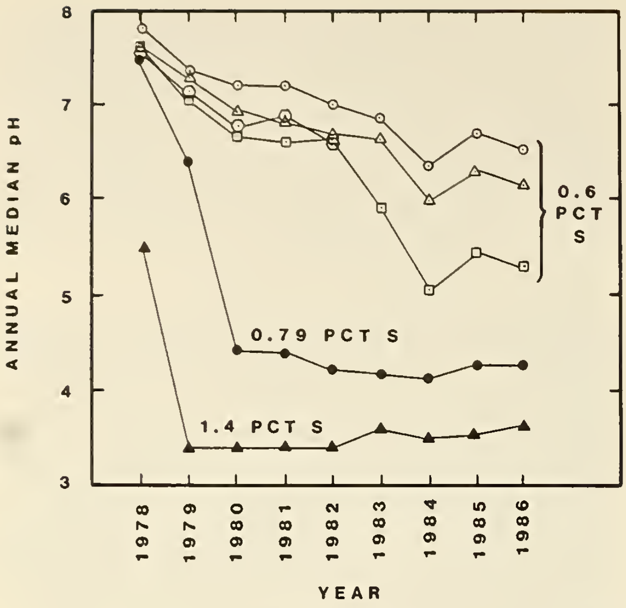

Figure 6.--Annual median pH values of test stockpile drainage from 1978 to 1986 (modified from Eger and Lapakko 1985).

The pH decrease and concomitant trace metal concentration over time were observed in drainage from an operational scale stockpile at the LTV Dunka site near Babbitt, MN. A drainage denoted as Seep 1 flows from 1.5 million tons of stockpiled Duluth Complex rock removed from an open pit taconite mine. The stockpile was constructed in 1976 and drainage has been monitored since this time. From 1976 to 1986 the annual median pH decreased from 7.3 to 5.4 and annual median trace metal concentrations increased by factors of roughly 5 to 20 (Minnesota Department of Natural Resources 1988).

CONCLUSIONS

Ten Duluth Complex samples, obtained from core drilled by MINNAMAX exploration, were leached in a laboratory experiment. The number of samples was extremely small relative to the vast extent of the Duluth Complex. This experiment represents the starting point for examination of a wider compositional range, as well as the influence of other variables on the dissolution reactions.

The sulfur content of the samples examined ranged from 0.47 to 2.17 percent, the variation due largely to variable content of iron sulfides, in the form of pyrrhotite. Solids with sulfur contents of 0.8 percent or less produced neutral drainage while, with one exception, solids containing at least 0.92 percent S produced acidic drainage. The rate of iron sulfide oxidation, and the attendant acid production, increased linearly with sulfur content, consistent with first order dependence on available sulfide surface area. The rate of acid neutralization, which was controlled by silicate mineral dissolution, was relatively constant among the samples despite variations in the relative amounts of plagioclase, olivine, and pyroxenes present. This uniformity in neutralization rates adds credence to the possibility of predicting acid producing potential based on the sulfur content of Duluth Complex mining wastes, since they will be comprised primarily of these silicate minerals. At the 0.92 percent sulfur content, the rate of acid production due to iron sulfide oxidation exceeded the dissolution rate of silicate minerals which comprised 80 to 92 percent of the solid phase.

A solid containing 1.17 percent S did not produce acidic drainage since it contained about 3 percent calcium carbonate, or calcite, which is rare in the Duluth Complex (Stevenson et al. 1979). Unlike the silicate minerals, the calcite was able to neutralize the acid produced by the iron sulfide oxidation. The influence of this small mineralogical anomaly on drainage quality emphasizes the importance of examining the leaching behavior of numerous samples. Only then can leaching be described in terms of more general characteristics, such as sulfur content.

The laboratory leaching results were consistent with field observations on the variation of pH with respect to percent sulfur and time. The range of 0.8 to 0.92 percent sulfur in the laboratory appeared to be similar to a bulk sulfur content of approximately 0.6 percent for stockpiled rock. The drainage chemistry of stockpiles appears to be strongly influenced by the small particle size fraction, in which the softer sulfide minerals are concentrated. In conjunction with an elevated specific surface area, this produces a high sulfide surface area available for chemical reaction.

The equilibration period for the drainage pH is variable, and the experimental time frame must allow for steady state to be reached. Under field conditions, the drainage pH from three gabbro stockpiles containing 0.6 percent S has decreased for nine years, indicating that equilibrium has not yet been reached. Drainage pH from a stockpile containing 0.8 percent S approached apparent equilibrium after two years, while about one year was required for 1.4 percent S rock.

Although the pH dependence for test stockpiles was not as strong as that observed in the laboratory, trace metal concentrations increased as pH decreased. Projections based on the first year of drainage from these stockpiles would have underestimated subsequent release of acid and trace metals by at least two orders of magnitude (Eger and Lapakko 1985). The decrease in pH and attendant increase in trace metal concentrations was also observed in drainage from operational scale stockpiles. This temporal pH decline and trace metal concentration increase underlines the importance of allowing adequate reaction time for steady state to be approached.

Acknowledgements

The laboratory experiments were conducted by David Antonson, whose diligence and perceptiveness improved the experimental efficiency and accuracy. Albert Klaysmat, with assistance from Jean Drotts, was responsible for the prompt and precise chemical analysis of the solids and numerous drainage samples generated. Paul Pojar and Milan Dicklich contributed to the construction of the experimental apparatus. Permission for use of the drill core samples was granted by Kennecott Minerals Company.

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ACID MINE DRAINAGE AND MANAGEMENT OF EASTERN OIL SHALE RESOURCES AND ASSOCIATED WASTE PRODUCTS

Patrick J. Sullivan and Jennifer L. Yelton[1]

Abstract.--The objectives of this research were to 1) understand the chemistry of acid mine drainage associated with oil shale resources and 2) suggest appropriate management options to minimize water quality problems. In this study, two eastern oil shales were collected. Each shale was retorted and combusted to produce waste products representative of potential mining and energy conversion processes. Each raw, retorted, and combusted shale was studied under the following laboratory conditions; 1) oxidizing equilibrium, 2) oxidizing nonequilibrium, and 3) reducing equilibrium. The Experimental results show that 1) the fundamental chemical equations that have been used to predict acid mine drainage are not correct, 2) using the new equations developed in this study, fundamental thermodynamic constants can be used to predict major and minor element activities, 3) the acid-base account method is not adequate for predicting acid potential, 4) simulated weathering methods should be used to predict acid potential, 5) combusted shales do not produce acid drainage under all disposal conditions, and 6) mineral weathering prior to the disposal of raw shales will significantly influence the acid potential of a material. These results suggest the following management implications 1) it is possible to predict leachate chemistry from waste and site specific data using thermodynamic constants, 2) placing weathered raw shale in a saturated environment can result in acid drainage, and 3) shales with a negative acid-base account should be combusted to minimize acid potential.

INTRODUCTION

When geologic materials containing iron sulfides are exposed at the earth's surface, acid mine drainage may occur. Because many raw and processed oil shales contain iron sulfides suggests that these materials need to be characterized to determine their acid potential prior to mining or processing. This characterization is a critical step in selecting management methods for a specific waste and disposal environment to avoid water quality problems associated with low pH and high trace element concentrations (Martin 1974, Griffin 1980, Wahler 1978).

The extraction of eastern oil shale resources is a critical concern, since these shales contain iron sulfides. In addition to the raw shales, retorted and combusted oil shales may also contain iron sulfides (Paciorek et al. 1984). Each of these materials will generate a leachate that reflects the mineral properties of each shale and selected disposal environment. The ability to characterize both acid potential and trace element release of each shale in a selected environment begins with understanding the chemical reactions that are commonly used to describe iron sulfide oxidation.

Theory of Acid Generation

In a natural aerobic environment, iron sulfide compounds have the potential to oxidize and produce acidity. The best example of this natural process is the oxidation of FeS_2 (pyrite) that usually occurs in mining wastes, coal cleaning waste, spoil, and acid sulfate soils (Smith et al. 1974). The oxidation of pyrite in a natural environment is suggested by the following reactions (Stumm and Morgan 1981).

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ + \qquad (1)$$

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \qquad (2)$$

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$$Fe^{3+} + 3H_2O = Fe(OH)_{3(s)} + 3H^+ \quad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

After pyrite is oxidized by atmospheric oxygen (eq 1), ferric iron is produced extremely slowly (eq 2). This second reaction, however, can be accelerated by microbial catalysis (aerobic) to increase the overall rate of ferrous iron oxidation. With the generation of ferric iron, insoluble ferric hydroxide may form (eq 3). Pyrite can also be oxidized by soluble ferric iron (i.e., in saturated or unsaturated environments), resulting in the generation of more acidity and ferrous iron (eq 4).

With iron sulfide oxidation, Nordstrom (1982) proposes the formation of secondary iron phases that include ferrous iron sulfates, ferric iron sulfates (jarosite), and other ferric iron hydroxides and oxides. However, Nordstrom (1982) does not quantitatively show the environmental conditions in which these specific solid phases may be generated. Once these compounds are formed, Sullivan and Sobek (1982) have shown that soluble acidity in the form of ferric and ferrous iron will be released to solution. This is especially critical in evaluating the influence of geochemical weathering of iron sulfides prior to disposal.

Research Objective

Based on the discussion above, the objectives of this two-year study were to characterize the acid production of eastern oil shale waste products (i.e., raw shale fines, retorted shale, and combusted shale) as a function of process conditions, waste properties, and disposal practice and to recommend management practices. In order to understand acid production, each waste was characterized by determining the acid-base account and laboratory weathering studies to assess its acid potential and chemistry.

DESCRIPTION OF RESEARCH

Oil Shale Selection

A high pyrite shale, selected from the U.S. Department of Energy's reference shale E86, was collected by Terra Tek. The sample was collected from an unweathered section of the upper part of the New Albany Shale of the Borden Formation located in Bullitt County, KY. A shale with a low concentration of pyrite was collected from a weathered outcrop of the Chattanooga Shale located in the Chestnut Mound section of Smith County, TN.

Oil Shale Processing

Both oil shales were crushed to pass a 3-inch screen. All particles passing a 1/2-inch screen were rejected from the feedstock. Each feedstock was 1) retorted using the indirect-heated Paraho process by Western Research Institute and 2) combusted using a fluidized bed process by J&A Associates. When both shales were retorted by the Paraho process and were indirectly heated to 500°C for 12 minutes, the spent New Albany Shale retained 80% sulfur and had 28% organic carbon conversion. The spent Chattanooga Shale retained 76% sulfur and had a 26% organic carbon conversion when these shales were also combusted using a fluidized bed reactor in air at 760°C for 15 minutes, the combusted New Albany Shale retained 43% of the sulfur and had an 87% organic carbon conversion. The combusted Chattanooga Shale retained 81% of the sulfur and had an 83% organic carbon conversion. The details of the retorting and combustion activities are given in Sullivan et al. (1987).

Laboratory Characterization

The acid-base account was determined for each shale using the method as given by Sobek et al. (1978). Laboratory studies were designed to simulate the following disposal environments, 1) oxidizing nonequilibrium leaching, 2) oxidizing equilibrium, and 3) reducing equilibrium. All solutions generated from these laboratory studies were analyzed for the following: pH, Eh (as mv), cations by ICP (Al, Ba, Ca, Cd, Co, Cu, Na, Fe, K, Mg, Mn, Ni, Pb, Sr, Zn) and anions by ICP and IC (As, Cl, Mo, S, Sb, Se, Si).

Oxidizing Nonequilibrium Studies

The humidity cell, developed by Caruccio (1968), can be used to simulate natural weathering of iron sulfides in an aerobic unsaturated environment. In this method, acid production will occur due to sequential leaching that allows oxidizing conditions to exist in a moist environment. In this study, the following humidity cell procedure was used. One kilogram of each shale (<2.00mm) was evenly spread out in the humidity cell, and the lid was tightly sealed. Dry air was passed over the samples for three days. From day four to day seven, humidified air was passed over the samples. On the seventh day, one liter of distilled-deionized water was added to each cell and allowed to equilibrate for one hour. After that time period, the solutions were extracted, filtered, and the sediments were returned to each respective cell. This cycle continued for 19 weeks. A solution of Thiobacillus ferrooxidans and Thiobacillus thiooxidans was added to each cell on the fifteenth week to increase acid production.

Oxidizing Equilibrium Studies

This method simulates waste disposal in a saturated groundwater environment that will be in contact with atmospheric oxygen (i.e., fluctuating watertable). In this environment, it is anticipated that the reaction in equation 1 will occur. However, the chemistry of the system will be determined by thermodynamic equilibrium conditions (i.e., no leaching).

Two hundred fifty-grams of each sample were placed into 500 mL Nalgene plastic bottles. Two hundred fifty milliliters of distilled-deionized water were added to these bottles and were capped tightly. A plastic tube was inserted through the cap to the bottom of the bottle to supply a constant flow of compressed air. Each sample bottle was placed into a water shaker bath at a constant temperature of 25°C. The samples were shaken at a constant rate of 60 rpm and were agitated manually four times a week. One bottle for each shale was removed from the water bath for analyses after 1, 4, 8, 16, 32, 64, 128, and 180 days of equilibration time. The samples were filtered, and the clear filtrates were analyzed for pH, Eh, and total acidity and alkalinity and split for analyses. Samples saved for anion analysis were kept at 4°C, and those saved for metals analysis were adjusted with concentrated HNO_3 to a pH <2.

Reducing Equilibrium Studies

This method simulates waste disposal in groundwater conditions that would have limited contact with atmospheric oxygen. It would be expected that little or no oxidation of pyrite would occur from equation 1. However, it is anticipated that acid production could occur as a result of the reaction given in equation 4. There is no leaching so that chemical equilibrium will be established.

Two hundred fifty-grams of each sample were placed into 500 ml Nalgene plastic bottles. Two hundred fifty milliliters of distilled-deionized water were added to these bottles and were capped tightly and taped to limit oxygen diffusion into the bottle. Each sample bottle was placed into a water shaker bath at a constant temperature of 25°C.

The samples were shaken at a constant rate of 60 rpm and were agitated manually four times a week. One bottle for each shale was removed from the water bath for analyses after 1, 4, 8, 16, 32, 64, 128, and 180 days of equilibration time. The samples were filtered and the clear filtrates were analyzed for pH, Eh, and total acidity and alkalinity and split for analyses. Samples saved for anion analysis were kept at 4°C, and those saved for metals analysis were adjusted with concentrated HNO_3 to a pH <2.

RESULTS AND CONCLUSIONS

Potential Acidity

The results of the acid-base account are given in Table 1. These data show that the raw New Albany Shale, raw Chattanooga Shale and the retorted Chattanooga Shale have the potential to produce an acid mine drainage problem. Based on the work of Ferguson and Erickson (1986), it would also be predicted that these same materials would produce acidity in a field environment (i.e., acid-base account <+33).

Table 1.--Acid-base account of raw and processed shales.

Waste	%FeS-S	Acid	Base	Balance*
		(Tons of $CaCO_3$/1000 tons of waste)		
Raw NAS	4.2	-131.3	4.9	-126.4
Retorted NAS	0.08	-2.5	65.0	62.5
Combusted NAS	0.04	-1.3	226.0	224.7
Raw CS	1.9	-58.4	24.1	-34.4
Retorted CS	0.8	-25.0	22.8	-2.2
Combusted CS	0.6	-18.8	170.9	152.1

* (-) indicates a net acid potential
NAS=New Albany Shale, CS=Chattanooga Shale

Humidity Cell

The humidity cell data represent a weathering environment that would stimulate maximum acid potential of a material. Humidity cell pH as a function of time is given in figure 1 for the New Albany Shale and the Chattanooga Shale in figure 2. These data clearly show that the New Albany and raw and spent Chattanooga Shales will produce acid leachates. This suggests that these materials can produce acid mine drainage in an unsaturated surface disposal environment.

When these data are compared to the acid-base account values of each shale, only the spent New Albany Shale was predicted to have a non-acid leachate (even in a field environment, i.e., value >+33). This suggests that the sources of neutralization in the spent shales were overestimated and/or not available for neutralization reactions during weathering.

During initial leaching (first 28 days), the raw Chattanooga Shale shows an acid pH and decreases rapidly. The raw New Albany Shale, however, demonstrates an initial neutralization and a steady decrease in pH. Because the raw Chattanooga Shale was weathered (but a lower concentration of pyrite than the New Albany Shale), some soluble acidity was released to show an acid pH with little available alkalinity.

Both retorted shales contain small concentrations of pyrite and both exhibit acid producing potential. After approximately 80 days, both shales establish a leachate pH below 4.0 after a loss of alkalinity. The combusted shales show a consistent decrease in pH with time. Like the retorted shales, the combusted shales have a small concentration of pyrite. However, because limestone was added to the combustion process, the combusted shales contain a higher neutralization potential. As a consequence, the leachate pH tends to remain higher. Even with this increased alkalinity, sulfide oxidation and dissolution of atmospheric carbon dioxide decreases leachate pH. When the pH was firmly established below 4.0 in the raw and retorted shales, microorganisms were added to the humidity cells. With this addition, the pH in both raw shales approached 2.0 (i.e., due to the increased rate of ferrous iron oxidation; equation 2). A corresponding rapid decrease of leachate pH associated with the retorted shale was not as evident due to a much lower concentration of sulfides.

Oxidizing Equilibrium

In the simulated oxidizing groundwater environment, it is assumed that the flow rate of groundwater in contact with a specific waste material will be slow enough to establish chemical equilibrium. Since leaching does not occur in this system, pH will be controlled by secondary mineral formation and hydrolysis but not iron sulfide oxidation. The oxidizing equilibrium pH as a function of time for the New Albany Shale is given in figure 3 and for Chattanooga Shale in figure 4.

The data for the raw shales show that the pH of the Chattanooga Shale extract is acidic and becomes more acidic with time, while the pH of the New Albany Shale extracts become alkaline and then pH decreases.

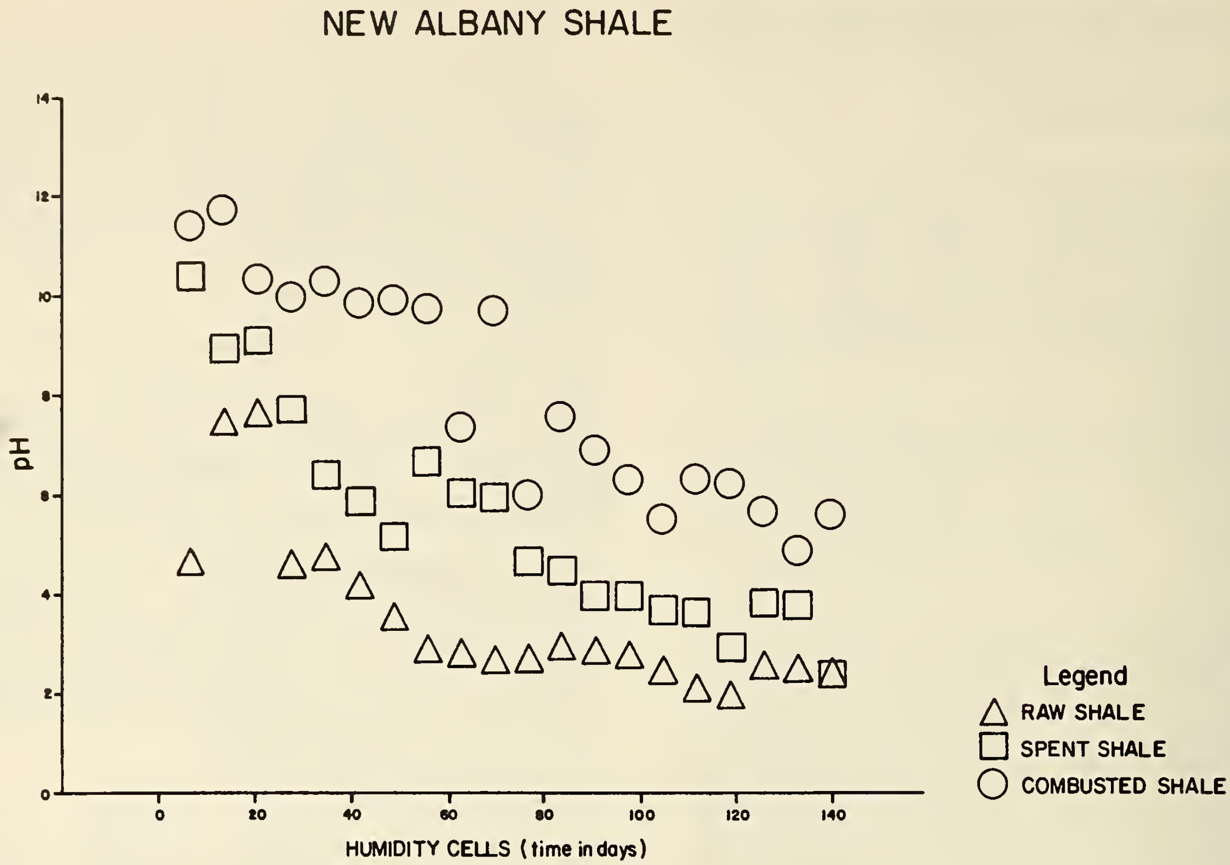

Figure 1.--pH data for the New Albany Shale humidity cell extracts.

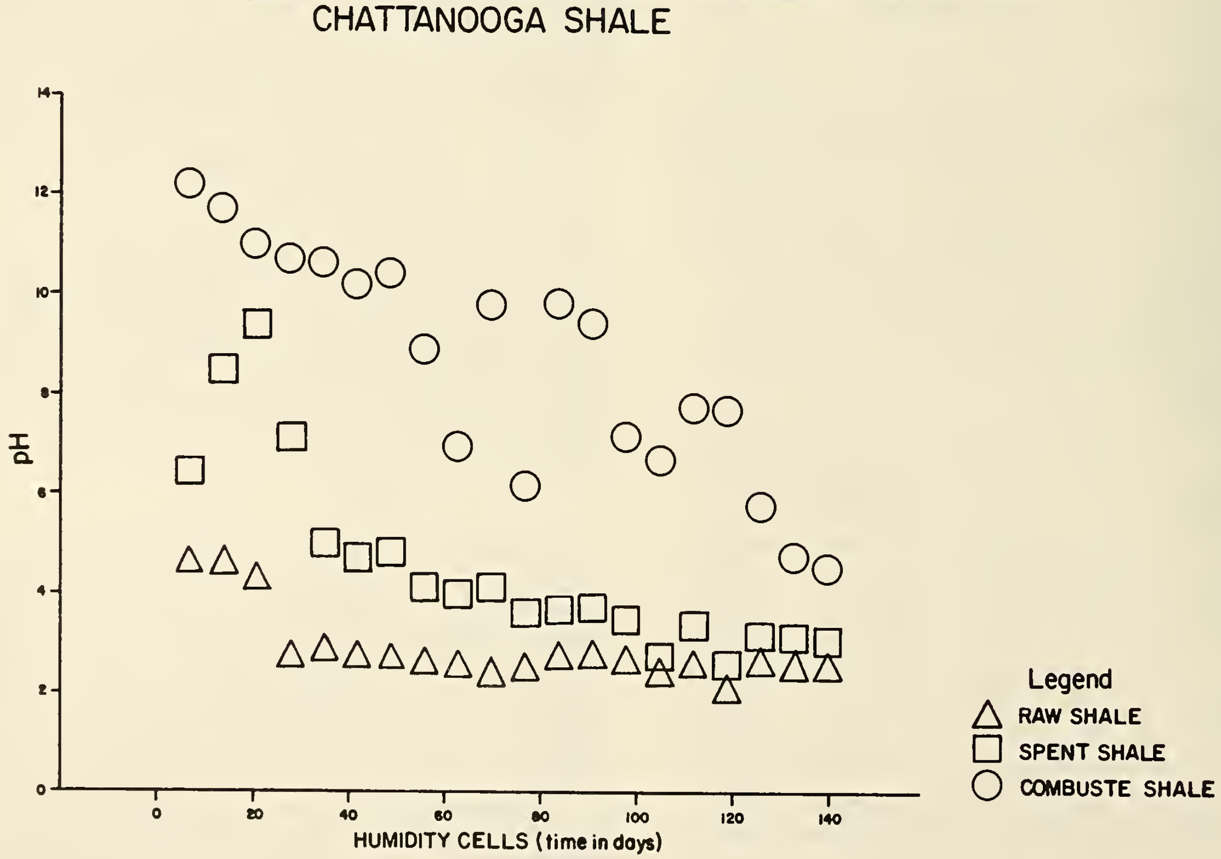

Figure 2.--pH data for the Chattanooga Shale humidity cell extracts.

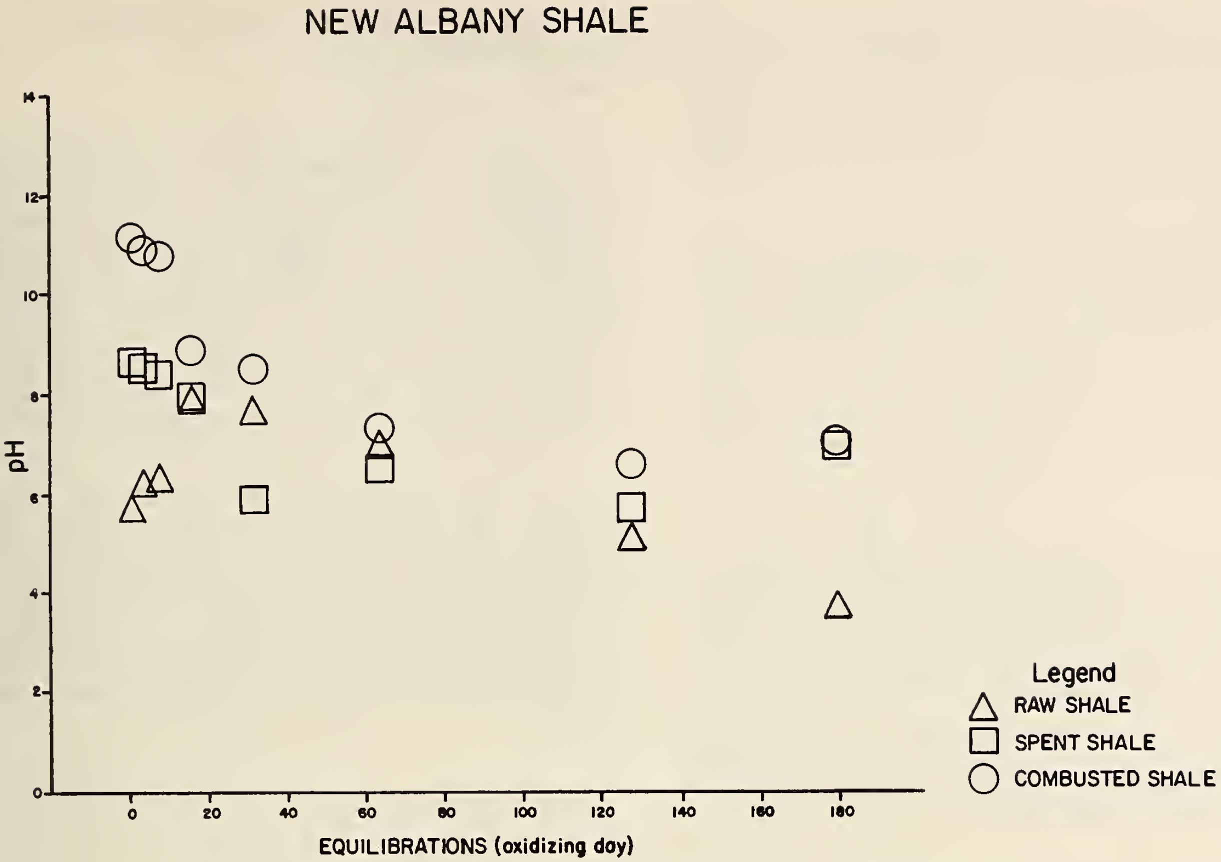

Figure 3.--pH data for the New Albany Shale oxidizing equilibrium extracts

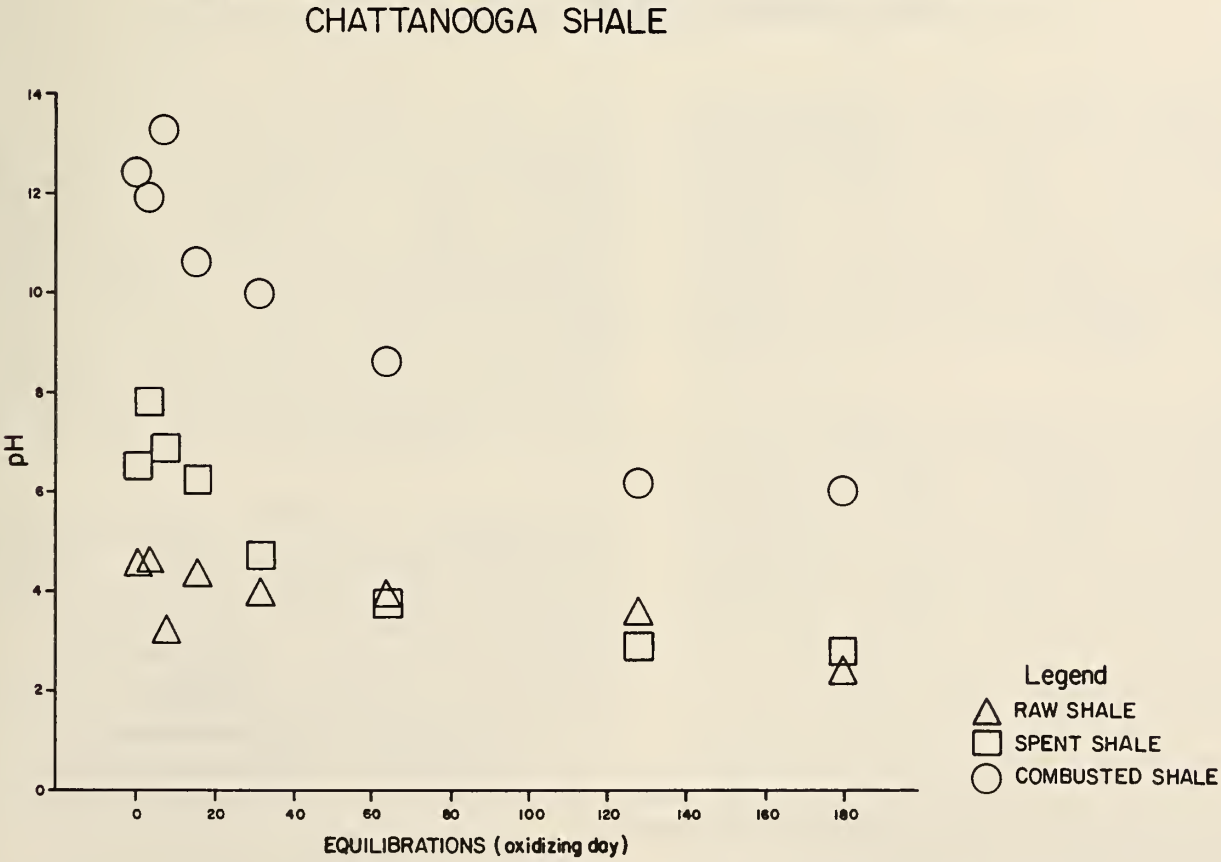

Figure 4.--pH data for the Chattanooga Shale oxidizing equilibrium extracts.

This once again demonstrates the influence of mineral weathering prior to disposal (and not the concentration of pyrite). Both final pH values are still very low but not to the same degree as the humidity cell leachates. However, these data still support the fact that these raw shales will produce acid mine drainage if they occur in a similar groundwater environment.

The retorted Chattanooga Shale also exhibits a pH trend that will eventually produce acid mine drainage; however, the New Albany Shale does not exhibit the same trend. Unlike the humidity cell, there is more time for neutralization reactions to occur. Since the retorted New Albany Shale has a greater neutralization potential than the retorted Chattanooga Shale, this trend is not unexpected. These data correspond more closely to the predicted acid potential as indicated by the acid-base account.

The pH of all combusted shale solutions remains fairly alkaline to 180 days. Even with potential iron sulfide oxidation and recarbonation, the pH tends to remain high due to a greater concentration of alkaline materials (note: the combusted New Albany Shale has a higher neutralization potential than the combusted Chattanooga shale).

In this simulated environment, the acid-base account method more accurately predicts acid-producing potential. However, it still does not indicate the hazard of mineral weathering and soluble acidity.

Reducing Equilibrium

In the simulated reducing ground water environment, it is assumed that 1) the flow rate of groundwater in contact with a specific waste material will be slow enough to establish chemical equilibrium and 2) atmospheric oxygen will not influence solution chemistry. Like the oxidizing equilibrium studies, leaching does not occur in this system, so pH will be controlled by secondary mineral formation and hydrolysis and not iron sulfide oxidation. The reducing equilibrium pH as a function of time for the New Albany Shale is given in figure 5 and for Chattanooga Shale in figure 6.

The data for the raw shales show that the pH of the New Albany Shale extracts remains just slightly acidic, while the Chattanooga Shale extracts are very acidic. This trend, once again, shows how soluble acidity can influence solution chemistry without pyrite oxidation. In the absence of 1) an atmospheric influence on solution chemistry and 2) leaching, retorted and combusted shale solutions does not generate acid mine drainage.

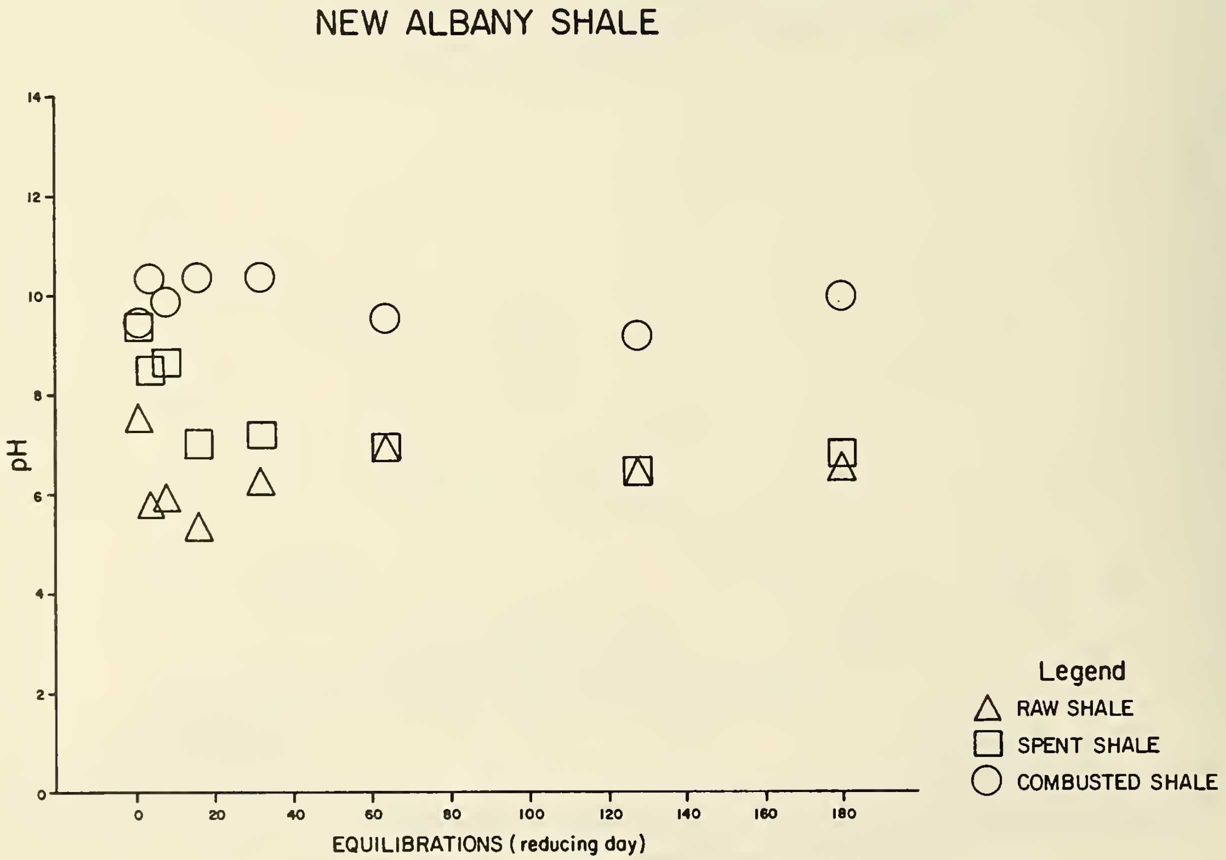

Figure 5.--pH data for the New Albany Shale reducing equilibrium extracts.

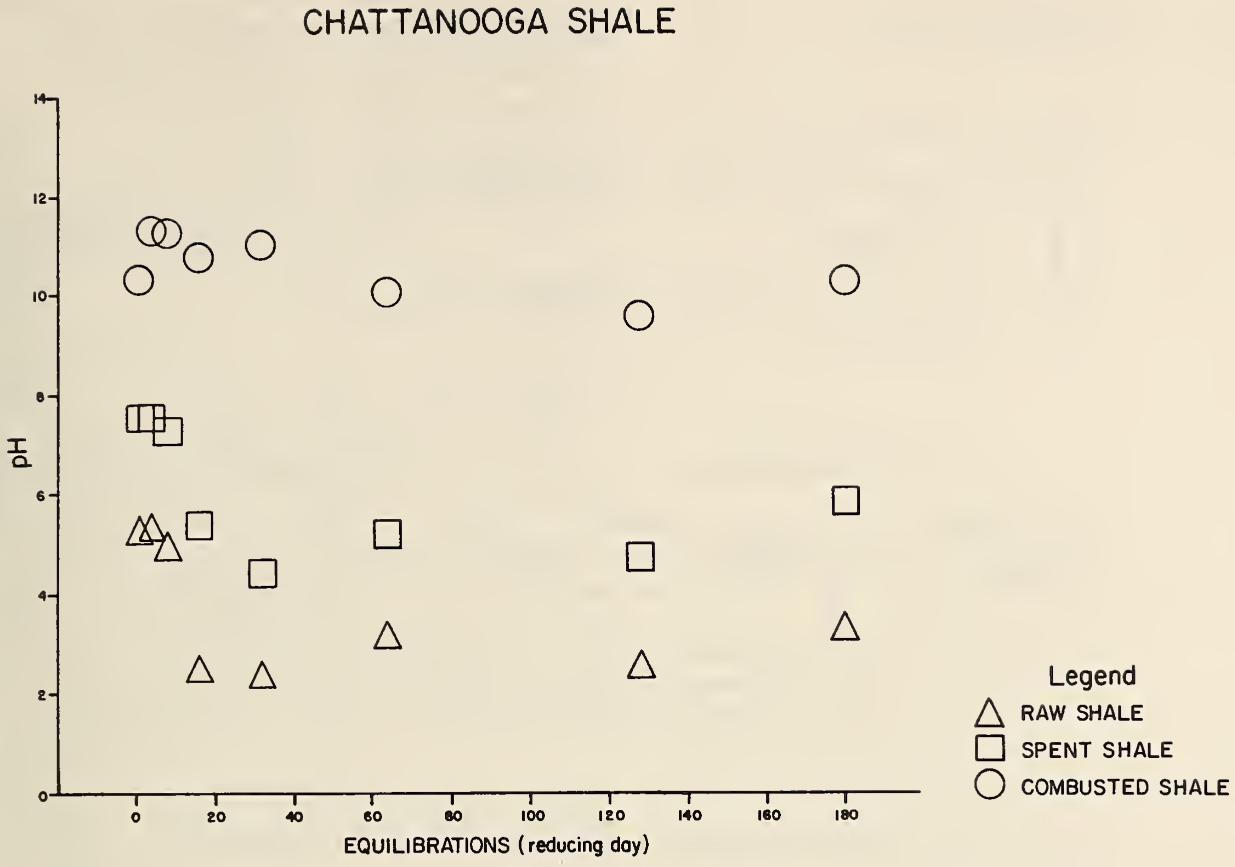

Figure 6.--pH data for the Chattanooga Shale reducing equilibrium extracts.

Generation of Acidity

All total chemical analyses from each study were coded and speciated with the WATEQFC geochemical code (Runnells and Lindberg 1981) to calculate ion activities. Based on this speciation, the minerals that control iron and aluminum solubility in acid mine drainage solutions were determined. The results of this analysis are given in Sullivan, et al. (1988). The equations that control iron and aluminum solubility are given in figure 7 (Sullivan et al. 1988). The results of this study demonstrate that below a pH of 6.00, the activities of Fe^{3+} and Al^{3+} are controlled by basic sulfate solid phases. This shows that equations 3 is not valid below a pH of 6.00.

In addition, there is a significant interaction between Al^{3+} and SO_4^{2-} influencing acid generation. Thus, the equations describing acid production associated with pyrite oxidation below a pH of 6.00 (most acid mine drainage is well below pH 6.00) should include the following reactions: In aqueous solutions below pH 6.00, $AlOH^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $FeOH^{2+}$, $Fe(OH)^{2+}$, and $Fe_2(OH)_2^{4+}$ are the predominant ionic species. This suggests that at chemical equilibrium, pH will be a function of Al^{3+} and Fe^{3+} hydrolysis.

Predicting Aqueous Chemistry

In a disposal environment, the rate of infiltration or ground water flow will influence the aqueous chemistry. If waterflow is slow enough to allow contact times necessary to establish equilibrium (i.e., rate of reaction faster than the flow rate through the system), the water quality characteristics will reflect the influence of secondary mineral formation. With increased leaching rates and rapid removal of reaction products, the kinetics of mineral dissolution-precipitation and adsorption will determine water quality characteristics. This may result in a nonequilibrium or metastable equilibrium condition influencing the aqueous chemistry.

If the waste/water system is at chemical equilibrium and the aqueous chemistry can be defined by secondary mineral reactions, then any leachate that leaves the disposal environment can be predicted using fundamental thermodynamic constants. With these fundamental relationships established, waste-specific/site-specific test methods can be used to predict water quality as a function of disposal site design (i.e., design which influences waste composition and flow rate).

If water quality predictions are not acceptable, then treatment options can be included in the test procedure.

Manage Acid Mine Drainage

It is clear from the weathering study data that the acid-base account should be used as the first step in determining acid potential.

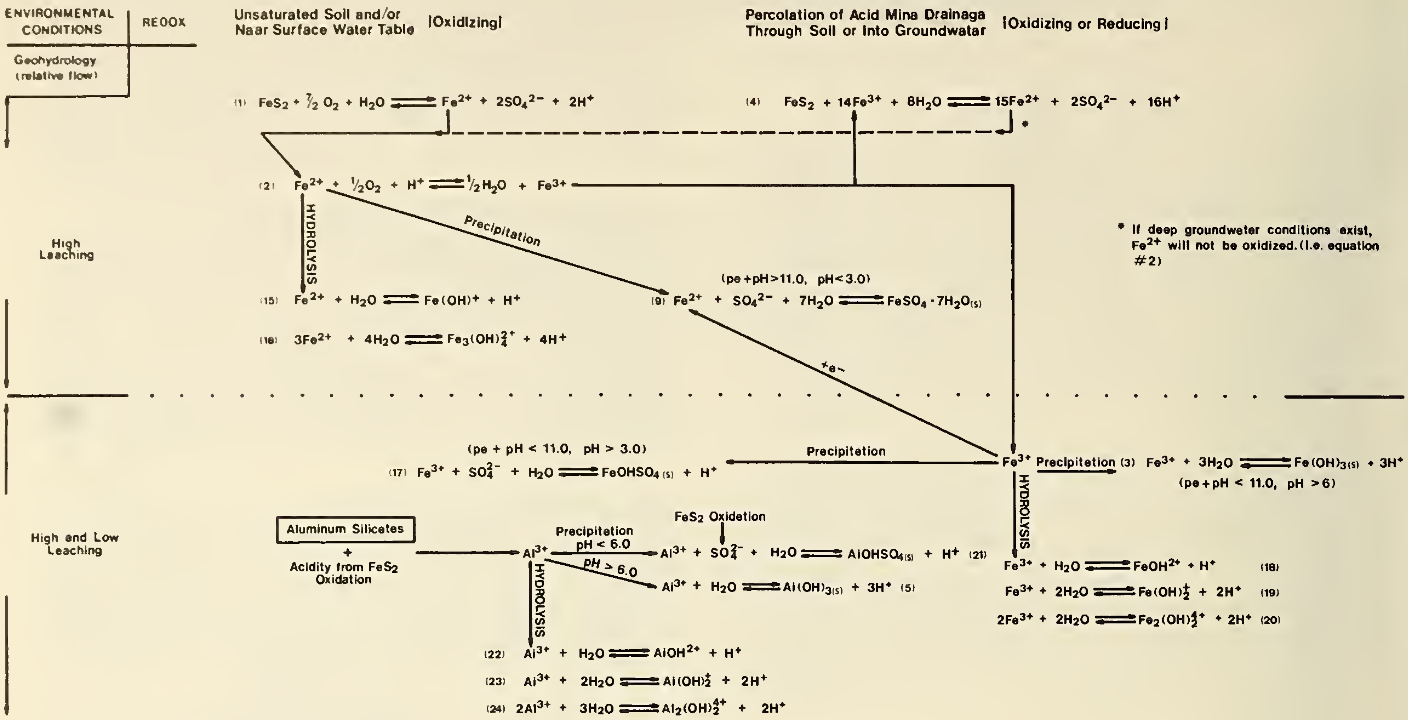
ENVIRONMENTAL CONDITIONS
REDOX
Geohydrology (relative flow)
Unsaturated Soil and/or Near Surface Water Table
(Oxidizing)
Percolation of Acid Mine Drainage Through Soil or Into Groundwater
(Oxidizing or Reducing)
(1) FeS2 + 7/2 O2 + H2O ⇌ Fe2+ + 2SO4 2- + 2H+
(4) FeS2 + 14Fe3+ + 8H2O ⇌ 15Fe2+ + 2SO4 2- + 16H+
(2) Fe2+ + 1/2O2 + H+ ⇌ 1/2H2O + Fe3+
High Leaching
HYDROLYSIS
Precipitation
* If deep groundwater conditions exist, Fe2+ will not be oxidized. (i.e. equation #2)
(pe+pH>11.0, pH<3.0)
(15) Fe2+ + H2O ⇌ Fe(OH)+ + H+
(9) Fe2+ + SO4 2- + 7H2O ⇌ FeSO4·7H2O(s)
(16) 3Fe2+ + 4H2O ⇌ Fe3(OH)4 2+ + 4H+
+e-
(pe + pH < 11.0, pH > 3.0)
(17) Fe3+ + SO4 2- + H2O ⇌ FeOHSO4(s) + H+
Precipitation
Fe3+ Precipitation (3) Fe3+ + 3H2O ⇌ Fe(OH)3(s) + 3H+
(pe+pH < 11.0, pH >6)
High and Low Leaching
Aluminum Silicates
+
Acidity from FeS2 Oxidation
FeS2 Oxidation
Precipitation pH < 6.0
pH > 6.0
Al3+ + SO4 2- + H2O ⇌ AlOHSO4(s) + H+ (21)
Al3+ + H2O ⇌ Al(OH)3(s) + 3H+ (5)
Fe3+ + H2O ⇌ FeOH2+ + H+ (18)
Fe3+ + 2H2O ⇌ Fe(OH)2 + + 2H+ (19)
2Fe3+ + 2H2O ⇌ Fe2(OH)2 4+ + 2H+ (20)
(22) Al3+ + H2O ⇌ AlOH2+ + H+
(23) Al3+ + 2H2O ⇌ Al(OH)2 + + 2H+
(24) 2Al3+ + 3H2O ⇌ Al2(OH)2 4+ + 2H+

Figure 7.--Acid generation equations from Sullivan, Reddy, and Yelton (1988).

With the completion of these tests, all samples with an acid-base balance <+33 should be tested using a weathering method that best simulates the disposal environment. It is also clear that more rapid weathering methods for determining potential acidity need to be developed.

These data suggest that raw shales which are allowed to weather and generate soluble acidity may produce acid conditions in a saturated system. This demonstrates the need to evaluate leachate chemistry prior to disposal if shales are allowed to weather. The most significant result of this study is that combusted shales will not produce an acid leachate. Thus, shales with an acid-base account balance <+33 could be combusted prior to disposal. This could significantly reduce water quality problems and eliminate long-term water treatment costs.

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EVALUATION OF THE TCLP METHOD FOR TWO MILL TAILINGS[1]

John C. Franklin and Eric G. Zahl[2]

Abstract.--Initial results are reported on determining the applicability of the toxicity characteristic leach procedure (TCLP) in predicting the potential for heavy metal contamination associated with mining wastes. TCLP tests, variations of the TCLP tests, and baseline tests were run on tailings samples from two mills to determine the sensitivity of laboratory protocol to slight procedural errors and to determine if any inherent factors produced a fatal flaw in using the test to evaluate mine tailings. Results from tailings A showed that metal ion concentration increased with higher liquid-to-solid ratios, with an increased volume of HOAc, and with longer mixing times. Results from tailings B showed the same general trends, but varied significantly in sensitivity to variations. The average yield of the standard TCLP tests as a percentage of the total digestion assay is 20% for tailings A and 10% for tailings B. This is a significant difference between the two types of tailings. Evaluation of these initial results indicates that the sensitivity of the three parameters to laboratory errors is probably acceptable if laboratory procedures are followed with normal attention to detail. These results are only the initial phase of a systematic evaluation of the TCLP method. Future research should emphasize how well the TCLP test actually simulates mine waste contamination phenomena. In particular, studies should focus on the applicability of the extraction fluid, chemical and mineralogical effects in and around the disposal area, time, pH effects, and oxidation effects.

INTRODUCTION

Substantial public concern has been voiced regarding contamination of water resources caused by mining (non-coal) and resulting adverse effects on human health. This concern has prompted the Environmental Protection Agency (EPA) to initiate a regulatory development program for the mining industry, which in turn has created a need to predict contamination potential at mine sites (EPA-December 1985 Report to Congress). Members of the American Mining Congress, the mining industry's most prominent collective organization, have stated that resolution of the mining waste problem is the mining industry's number one issue. Regulatory efforts under the Resource Conservation and Recovery Act (RCRA) initially utilized the EP toxicity test as a primary standard with which to evaluate contamination potential (EPA-Office of Solid Waste 1987). This test was selected for analyzing metal mine wastes since its use is standard practice in determining whether industrial wastes are categorized as hazardous and unacceptable waste for sanitary landfills. However, there have been many technical concerns about its applicability to mining wastes. These concerns have centered mainly around the assumptions inherent in the testing procedures; that is, certain assumptions cause the test to be a poor simulator of mine waste disposal conditions. For example, the preferential dissolution of lead by the acetic acid used in the test procedures skews tests for lead, a heavy metal of great importance in mining wastes (Lead Industries Association Report 1984).

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As a result, the U.S. Bureau of Mines' Spokane Research Center (SRC) is performing research to determine more effective methods of evaluating the potential for contamination due to metal/nonmetal mining activity. As part of this effort, we are examining existing laboratory testing methods to determine what applicability they may have in assessing contamination potential. The first test now in the process of being reviewed is EPA's toxicity characteristics leach procedure (TCLP) (Federal Register, Volume 51, No. 9). This method was selected since it is currently being considered as a replacement for the EP toxicity test. Also, EPA is actively seeking evaluation methods for its Mine Waste Regulatory Development Program and it has been suggested that the TCLP method could be utilized.

This report examines the results of tests using the TCLP method for monitoring metal contamination from mill tailings from two different mills. Organics and volatiles were excluded from these experiments because they are of little concern in mine tailings. Eleven key elements were analyzed. Some modifications were made to the standard TCLP method in order to streamline laboratory procedures because there are no organics or volatiles to consider. For all tests, the organics testing portion was deleted and the leachant was filtered by gravity with a qualitative grade filter rather than by pressure or under a vacuum. Other experimental variations to the standard TCLP method were made as discussed below to evaluate the method.

MATERIALS AND METHODS

To determine what changes in metal concentrations would be seen in the TCLP test, the liquid-to-solid ratio, acid strength, and mixing time were varied. The standard TCLP test procedures require a liquid-to-solid ratio of 20:1, a volume of 5.7 mL of glacial HOAc (acetic acid) made up to 1 L of extraction fluid with ASTM type 2 water to obtain a molarity of 0.10 and a rotation time of 18 hours. The liquid-to-solid ratio was varied by using a standard sample of 50 of solid and varying the total volume of slurry from 0.25 to 2.00 L. The molarity of HOAc was varied in our tests from 0.05 to 0.20, and the duration of rotation from 1 to 25 hours.

Total digestion analyses and modified TCLP tests using distilled water as an extraction fluid were also performed and the results compared to TCLP results to provide an indication of the stringency of the procedure. Tailings from two different mills were evaluated in these experiments. The first mill processed silver ore primarily while lead and zinc were secondary ores (tailings A). The second mill processed lead ore (tailings B).

The analyses were conducted on an AA spectrometer for aluminum (Al), silver (Ag), calcium (Ca), cadmium (Cd), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), nickel (Ni), lead (Pb), and zinc (Zn). The tailings were not tested for organics or volatiles because the project is concerned with metal contamination only. Results reported here include only Al, Cu, Fe, Ni, Pb, and Zn because concentrations of the other elements were very low or the variations were insignificant. TCLP test results are normally presented in milligrams per liter of slurry. However, results of most of these tests were converted to milligrams per gram of solid for comparing with digestion assays. This conversion is made by using the equation

$$A = (B*C)/D \qquad (1)$$

where A = mg of contaminant in each g of waste,
B = mg/L of contaminant in solution,
C = total volume of solution, L,
and D = total g of solid used.

This reporting unit (mg/g) also provides a more conceptually clear method of describing the contaminant release from a given amount of waste material.

RESULTS

In the first set of experiments, both the liquid-to-solid ratio and the acid strength were varied for tailings A as shown in table 1. Fifty grams of tailings were used in each test and the volume of leachant was varied to obtain variations in the liquid-to-solid ratio. The data for tailings A show a general increase in metal concentrations (1) as

Table 1.--Leaching of metal ions from tailings A with varying molarity of acetic acid and volume of leachant, mg ion/g of solid waste.

Volume, L	Al	Cu	Fe	Ni	Pb	Zn
			0.05 Molar			
0.25.......	0.029	0.009	0.645	0.003	1.07	0.145
.50.......	.037	.024	1.08	.004	1.49	.149
.75.......	.040	.026	1.50	.005	1.84	.137
1.00.......	.044	.026	1.88	.005	2.13	.124
1.25.......	.044	.027	1.76	.005	2.15	.158
1.50.......	.047	.027	2.05	.005	2.21	.162
1.75.......	.051	.027	2.43	.005	2.01	.161
2.00.......	.053	.027	2.54	.005	1.92	.160
			0.10 Molar			
0.25.......	0.041	0.024	0.90	0.003	1.26	0.164
.50.......	.050	.026	1.50	.003	1.73	.160
.75.......	.057	.028	1.94	.003	2.12	.176
1.00.......	.063[1]	.029[1]	2.31[1]	.003[1]	2.49[1]	.180[1]
1.25.......	.064	.028	2.63	.003	2.39	.340
1.50.......	.065	.028	2.89	.004	1.86	.174
1.75.......	.064	.029	3.07	.004	2.54	.182
2.00.......	.067	.029	3.81	.004	2.80	.172
			0.20 Molar			
0.25.......	0.052	0.026	1.98	0.004	1.50	0.177
.50.......	.055	.028	2.83	.004	2.21	.171
.75.......	.058	.029	3.47	.004	2.25	.165
1.00.......	.062	.029	4.00	.004	2.69	.170
1.25.......	.064	.029	4.48	.004	2.79	.183
1.50.......	.067	.029	4.66	.003	2.75	.173
1.75.......	.066	.029	4.84	.003	2.94	.173
2.00.......	.070	.030	5.33	.003	3.04	.166

[1] Results using standard TCLP test parameters (0.10 molar, 1.0 slurry).

Table 2.--Leaching of metal ions from tailings B with varying acetic acid molarity and volume of leachant, mg ion/g of solid waste.

Volume, L	Cu	Fe	Pb	Zn
		0.05 Molar		
0.50.....	0.002	0.001	0.187	0.090
1.00.....	.008	.001	.528	.102
1.50.....	.010	.003	.480	.118
2.00.....	.013	.005	.612	.128
		0.10 Molar		
0.50.....	0.009	0.001	0.338	0.125
1.00.....	.013[1]	.010[1]	.562[1]	.129[1]
1.50.....	.014	.211	.674	.138
2.00.....	.015	.638	.641	.135
		0.20 Molar		
0.50.....	0.013	0.674	0.360	0.145
1.00.....	.011	.630	.720	.141
1.50.....	.016	1.58	.780	.154
2.00.....	.016	1.82	.896	.148

[1] Result using standard TCLP parameters (0.10 molar, 1.0 L of slurry).

the volume of leachant was increased (increased liquid-to-solid ratio) and (2) as the molarity or acid strength was increased for all three molarity groups except for Ni, which remained constant throughout the test.

For tailings B (table 2), the parameters were varied, but fewer liquid-to-solid ratio data were collected since the results from the first set of experiments indicated the variations in concentrations were small and continually increasing with liquid amounts so that the measurement intervals could be made larger. Aluminum and nickel are not reported here because concentrations were low and changes in values were insignificant. The same general trends in test results occurred in tailings B as in tailings A. Concentration of the metal ions increased with increasing volume (liquid-to-solid ratio) and with increasing molarity of acetic acid in the leachant.

In the third set of experiments, the mixing time parameter was varied for leachant in contact with tailings A (tables 3-6). The standard method calls for 18 hours of mixing by rotation at 30 rotations per minute. Four test containers were rotated and samples were taken from containers 1, 2, 3, and 4 at 1, 2, 3, and 5-hour intervals, respectively, for 25 hours. Multiple containers were used to determine if the removal of analytical samples during rotation influenced the results. Results showed that if the data are averaged for each element and container, there is good agreement among the four different interval times. This indicates that removal of analytical samples during rotation did not influence test results. It should be noted that leachate concentrations of Cu, and to a lesser extent Al and Ni, remained relatively constant for various durations of mixing, while those of the other ions (especially Fe) continued to increase as the duration of mixing increased.

The concentrations of the various metals obtained using the modified TCLP were compared with the total available metal concentrations in the tailings. Assays were performed by the U.S. Bureau of Mines, Albany Research Center. The results of the analyses are reported in table 7 for the six reported metals and represent the digestion assay concentration for each element in every gram of tailings.

Table 3.--Effect of mixing time on the amount of metal ions leached from tailings A, container 1, mg ions/g of solid waste.

Hours	Al	Cu	Fe	Ni	Pb	Zn
1.....	0.0406	0.0246	0.248	0.0028	1.86	0.132
2.....	.0584	.0256	.428	.0030	1.82	.138
3.....	.0490	.0264	.618	.0030	1.82	.146
4.....	.0478	.0264	.730	.0030	1.88	.146
5.....	.0484	.0266	.898	.0034	1.94	.150
6.....	.0490	.0266	1.11	.0034	2.08	.152
7.....	.0558	.0276	1.28	.0040	2.08	.154
8.....	.0568	.0274	1.46	.0036	2.22	.156
9.....	.0556	.0276	1.59	.0038	2.28	.160
10.....	.0508	.0270	1.73	.0040	2.18	.164
11.....	.0538	.0268	2.09	.0040	2.36	.164
12.....	.0546	.0274	2.24	.0040	2.40	.172
13.....	.0520	.0266	2.51	.0040	2.46	.174
14.....	.0514	.0272	3.10	.0042	2.54	.170
15.....	.0512	.0274	3.10	.0040	2.60	.172
16.....	.0500	.0270	3.10	.0036	2.56	.172
17.....	.0574	.0272	3.74	.0042	2.74	.178
18.....	.0556	.0272	3.89	.0040	2.60	.180
19.....	.0588	.0266	4.11	.0034	2.68	.182
20.....	.0602	.0266	4.51	.0034	2.72	.184
21.....	.0590	.0264	4.95	.0044	2.76	.182
22.....	.0684	.0258	5.53	.0042	2.80	.188
Ave....	.0538	.0267	2.41	.0037	2.34	.164

Table 4.--Effect of mixing time on the amount of metal ions leached from tailings A, container 2, mg ions/g of solid waste.

Hours	Al	Cu	Fe	Ni	Pb	Zn
2.....	0.0440	0.0256	0.400	0.0028	1.86	0.122
4.....	.0484	.0262	.736	.0032	1.88	.148
6.....	.0484	.0264	1.05	.0034	1.98	.146
8.....	.0574	.0272	1.59	.0038	2.16	.164
10.....	.0504	.0266	1.83	.0042	2.28	.158
12.....	.0536	.0274	2.11	.0044	2.32	.168
14.....	.0504	.0270	2.40	.0040	2.44	.168
16.....	.0500	.0270	2.74	.0056	2.46	.172
18.....	.0512	.0272	3.10	.0040	2.42	.176
20.....	.0530	.0268	3.38	.0034	2.60	.178
22.....	.0440	.0266	3.64	.0042	2.58	.176
24.....	.0530	.0266	3.84	.0040	2.56	.180
25.....	.0544	.0272	4.03	.0042	2.65	.182
Ave....	.0506	.0268	2.37	.0039	2.32	.164

Table 5.--Effect of mixing time on the amount of metal ions leached from tailings A, container 3, mg ions/g of solid waste.

Hours	Al	Cu	Fe	Ni	Pb	Zn
3.....	0.0488	0.0264	0.550	0.0026	1.82	0.150
6.....	.0490	.0268	1.03	.0034	2.00	.158
9.....	.0512	.0268	1.55	.0046	2.20	.164
12.....	.0532	.0272	2.13	.0040	2.44	.168
15.....	.0526	.0274	2.52	.0032	2.48	.170
18.....	.0496	.0274	2.97	.0040	2.48	.176
21.....	.0446	.0258	3.21	.0036	2.54	.180
24.....	.0518	.0270	3.64	.0038	2.54	.180
25.....	.0544	.0276	3.75	.0042	2.62	.182
Ave....	.0506	.0269	2.37	.0037	2.35	.170

Table 6.--Effect of mixing time on the amount of metal ions leached from tailings A, container 4, mg ions/g of solid waste.

Hours	Al	Cu	Fe	Ni	Pb	Zn
5.....	0.0492	0.0258	0.882	0.0034	1.88	0.148
10.....	.0504	.0258	1.74	.0032	2.26	.156
15.....	.0496	.0262	2.44	.0032	2.32	.160
18.....	.0488	.0258	2.89	.0034	2.36	.170
20.....	.0550	.0260	3.03	.0040	2.44	.170
25.....	.0514	.0260	3.45	.0040	2.38	.172
Ave....	.051	.026	2.41	.004	2.27	.163

Table 7.--Assay results for tailings A and B, mg/g, and standard TCLP results as a % of assay.

Tailings	Al	Cu	Fe	Ni	Pb	Zn	Ave.
A, mg/g (assay)......	0.199	0.141	68.1	0.015	5.41	1.60	
% TCLP is of assay..	32	20	4	20	36	10	20
B, mg/g (assay)......	.188	.318	27.7	.138	1.77	.934	
% TCLP is of assay..	6	4	0	4	30	14	10

Table 8.--Average of 10 standard TCLP tests for tailings A and B, mg/g and standard deviations (SD), and coefficient of variation (CV).

Tailings	Al	Cu	Fe	Ni	Pb	Zn
A.........	0.064	0.028	2.99	0.003	1.97	0.167
SD.......	.001	.0004	.284	.0004	.036	.016
CV.......	2	1	9	13	2	10
B.........	0.012	0.012	0.011	0.005	0.524	0.133
SD.......	.003	.0004	.003	.0004	.132	.005
CV.......	25	3	27	8	25	0

Table 9.--Metal concentrations using deionized water as leachant, ions/g of solid waste.

Tailings	Al	Cu	Fe	Ni	Pb	Zn
A........	0.0002	nd	nd	nd	0.0014	0.0050
B........	.0024	nd	0.0002	nd	.0018	.0004

nd - below detectable limits

Standard TCLP test results are compared to the baseline assay data in table 7. Note that tailings A had an average of 20% for the six metals while tailings B had an average of only 10%.

Ten individual analyses were made on both tailings samples to determine the statistical reliability of each metal concentration (table 8). The coefficient of variation was less than 15 for tailings A in most of the metal concentrations, while tailings B had three elements with a coefficient of variation of 25 or larger. However, concentrations of two of these three elements approached the detection limits of the spectrometer. There is good agreement between the 18-hour test (tables 3-6) and the data reported in table 8.

The leachability of these ions by rainwater may be considerably less than that inferred from TCLP results using 0.1M acetic acid as leachant. Results of a modified TCLP test in which 1 L of deionized water was mixed with 50-g samples of tailings A and B are reported in table 9. Significantly less amounts of each element were leached by the water.

As previously stated, mill A was processing silver ore while mill B was processing lead. Because the ores from the two mills were different, the mill waste reacted quite differently to testing. The principal minerals present in mill A waste were silica, galena, and sphalerite; the principal mineral from mill B tailings was dolomite with trace amounts of sphalerite, pyrite, and galena.

A major difference observed during our investigation of these two mill tailings samples was the change in pH during the mixing period. The TCLP requires a starting pH of 2.88 but, unlike the EP toxicity method, does not specify the ending pH. For all our tests, the pH was measured before adding the mill waste and after the 18-hour mixing period. The pH increased to about 3.7 for mill tailings

A and to 5.0 for mill tailings B. Such an increase would be expected.

In another series of tests for tailings A, liquid samples (ready for AA analysis) were used to evaluate the time affect of sample storage. The samples were stored at room temperature and rerun after 2 weeks and again after 3 weeks to determine if delayed analysis affected the results. The average of all 52 runs was determined for Fe, Pb, and Zn and compared to the data in table 8. The results showed less than 6% difference between any of the delayed samples as compared to the 10 runs reported in table 8, indicating little change because of the 3-week delay before the filtered samples were analyzed.

CONCLUSIONS

The current project is the first phase of a detailed evaluation of the TCLP test to determine what, if any, applicability the test has in evaluating mine wastes. An evaluation of the results shows that there are many factors that may influence the TCLP laboratory test. The following points summarize the research to date.

- The TCLP results are not highly sensitive to changes in the liquid-to-solid ratio, acid strength, and duration of mixing. Small laboratory measuring errors will not have a significant impact on TCLP test results unless gross errors are made.

- Variations of the length of mixing time for the TCLP test show that equilibrium conditions for metal concentrations are attained for only some elements during the standard 18 hours. Other metal concentrations were increased at varying rates, indicating that the TCLP test results may be arbitrarily biased for certain elements as influenced by the length of mixing time.

- The percentage of metals extracted using the TCLP method varied significantly between the two tailings tested (20% versus 10%). This may indicate a bias of the TCLP method to being influenced by the mineralogical properties of the waste, which are not leaching phenomena considered in the standard TCLP test.

- Further research is needed to determine the applicability of the TCLP test to mining waste. The scope of this initial effort was limited to two tailings sources and assessment of only a few factors that could influence the applicability of the TCLP test to mining wastes.

Based on these results and other similar research at SRC, it appears that better laboratory assessment methods could be developed that more appropriately aid in the simulation or prediction of contamination from mine wastes. This preliminary assessment was made because of the great diversity in mineralogy, geology, hydrology, processing, and disposal methods of different mines, and because an accurate assessment of the hazards posed by any individual mining waste site is very difficult. Even in instances where the same material is mined, the disposal of waste may produce significantly different contamination effects from site to site. Significant factors, such as the effects of geologic formations and the hydrogeology between the source of the contaminant and the potential point of impact, should be considered. Such an evaluation may require assessment methods other than laboratory tests, such as field geophysical surveys. It is critical that these factors be taken into account when developing an effective assessment method for evaluating potential contamination from mine wastes.

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A COMPARISON OF RESULTS FROM ACID-BASE ACCOUNTING VERSUS POTENTIAL ACIDITY MEASURED BY THE PEROXIDE OXIDATION OF WEATHERED AND UNWEATHERED SOILS CONTAINING PYRITE[1]

J. T. Ammons and P. A. Shelton[2]

ABSTRACT

Ammons, J. T. (1) and Shelton P. A. (2). ((1) University of Tennessee, Knoxville (2) Southern Illinois University at Carbondale). Fifty samples from weathered disposal area soils and forty-nine samples from unweathered overburden cores were analyzed using two laboratory methods to assess potential acidity. Total sulfur values (percent) were compared with potential acidity values by hydrogen peroxide oxidation (meqH+/100g). The percent total sulfur values for the unweathered samples (cores) ranged from 0.006 to 1.32 percent. Potential acidity by hydrogen peroxide oxidation ranged from 3.05 to 67.98 meqH+/100g. Total sulfur values for disposal area soil (weathered) ranged from 0.008 to 0.920 percent. Hydrogen peroxide oxidation values ranged from 0. to 52.34 meqH+/100g in the weathered disposal area soils. The coefficient of determination (r^2) comparing the two methods is 0.89 for the unweathered samples and 0.71 for the weathered samples. There is a positive correlation between the two methods for the unweathered (fresh) core samples. This relationship is less pronounced for weathered samples from the surface of the disposal areas.

INTRODUCTION

Laboratory procedures to assess potential acidity problems prior to mining or before major construction have been used in overburden analyses studies by many investigators (West Virginia University 1971, Smith et al. 1974; Smith et al. 1976; Ammons et al. 1983). These laboratory techniques allow for postmining landuse and post construction landuse planning and decision-making.

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[2] J. T. Ammons, Associate Professor, University of Tennessee, Knoxville and P.A. Shelton, Research Associate, Southern Illinois University at Carbondale.

Two laboratory procedures have been historically used to estimate the levels of acid-producing materials resulting from mining and construction activities. These procedures are acid-based accounting and determination of potential acidity by peroxide oxidation (Smith et al. 1974). In this study, samples were analyzed to compare these procedures over a wide range of total sulfur values. The samples were selected from fresh overburden cores and disposal areas along the divide section of the Tennessee Tombigbee Waterway in Tishomingo County, MS.

In 1971, West Virginia University compared these procedures using fresh overburden rock samples from surface mines and found a high correlation between the two tests. The same comparison was conducted on old minesoil samples and no consistent relationship was found between the two tests (WVU 1971).

During the excavation of the divide section of the Tennessee Tombigbee Waterway pyritic spoil material was excavated and deposited in the disposal areas. The lower part of the Eutaw formation (Cretaceous) contained lenses of pyrite concentrated in sandy nodules (Ammons et al. 1983).

Corps of Engineers personnel used the peroxide oxidation procedure onsite to access potential acidity of waterway slope soils and requested a comparison of acid-base accounting (as estimated from total sulfur) and the peroxide oxidation procedure (WVU 1971). Although acid-base accounting is less time consuming laboratory facilities are not always available to complete this procedure. This was the impetus to conduct a comparison of the two methods.

MATERIALS AND METHODS

Forty-nine samples from fresh overburden cores (unweathered) and fifty samples of disposal area soils (weathered) were selected for this study. Sulfur values ranged from 0.006 percent to 1.328 percent, representing the range of sulfur values reported the divided section of the waterway.

Total sulfur analyses (as part of acid-base accounting) were completed on all samples using an Automatic Sulfur Analyzer. All samples were ground to 60 mesh for laboratory analyses as described by Sobek et al. (1878).

Potential acidity by hydrogen peroxide was completed according to Smith et al. (1974) except for the following modifications. Blanks were not used because the stablizer present in the hydrogen peroxide will not allow the peroxide to decompose upon heating if no sample is present to catalyze the decomposition. This would result in interference from the peroxide (a weak acid) during the titration. Additionally, the carbonates and sulfates were not removed from the samples prior to oxidation. Leaching the samples is a time-consuming process, so the hydrogen peroxide analyses were completed under the same conditions used by Corps of Engineers personnel in the field.

RESULTS AND DISCUSSION

The total sulfur, millequivalents hydrogen per 100 grams of material, and final acid-base account (tons/1000 tons material $CaCO_3$ equiv.) for overburden core samples are shown in the table 1. Sulfur values ranged from 0.006 to 1.328 percent. Table 2 shows sulfur values ranging from .008 to .920 percent on selected disposal area samples. Sulfur values rarely exceeded 1.0 percent on disposal area soils because of the intense chemical oxidizing environment at the surface immediaely after placement.

The results of the comparison between total sulfur and potential acidity by hydrogen peroxide are illustrated in figures 1a-b. The results of the fresh cores samples (fig. 1b) show a significant correlation (r^2=0.89) between the two methods. Figure 1a shows the results of the two methods on weathered disposal area samples. The relationship is less pronounced (r^2=0.71), suggesting interference in the peroxide procedure from some weathering products (fig. 1a).

Figures 2a-b present the results of the peroxide procedure compared with acid-base accounting. Acid-base accounting is reported in calcium carbonate equivalent (tons/1000 tons material) and includes neutralization potential (amount of bases present).

Table 1.--Total sulfur, milliequivalents of hydrogen by peroxide oxidation, and acid-base account of samples from overburden cores, Tennessee-Tombigbee Waterway.

Sample Number	Percent Sulfur	Meq H^+/ 100 G	Acid-Base Account $CaCO_3$ Equivalent Tons/1,000 Tons Material
895-14	1.3280	67.98	-45.12
895A-11	1.2800	51.40	-23.11
897-22	1.2350	43.33	-57.75
895-23	1.0620	46.61	-24.19
897-21	1.0400	35.96	-43.04
897-34	0.8894	4.97	-28.25
897-36	0.8573	16.36	-16.08
895-26	0.7820	33.45	-21.37
894-30	0.7495	29.82	-24.65
894-5	0.7108	33.16	-25.17
897-51	0.6488	30.62	-30.13
894-33	0.5532	23.91	-19.75
894-19	0.5496	8.80	-22.35
897-23	0.5481	24.47	-23.14
897-41	0.5398	18.01	-24.96
895-35	0.5268	22.73	-19.67
894-6	0.5090	21.97	-22.81
897-20	0.4903	17.13	-18.62
896-42	0.4884	20.38	-15.95
895-38	0.4632	17.28	-12.26
894-14	0.4504	20.48	-14.08
894-38	0.4375	20.05	-17.12
894-34	0.4136	17.43	-14.65
894-44	0.4074	14.64	-14.45
894-3	0.3904	18.92	-14.66
894-36	0.3794	15.98	-13.58
896-34	0.3470	14.07	- 8.32
897-13	0.3333	14.73	-11.97
895-10	0.3078	12.95	- 9.29
897-47	0.2859	9.24	-10.85
895A-12	0.2749	10.68	- 8.47
894-15	0.2623	9.54	- 7.21
895A-9	0.2522	11.14	- 7.06
894-28	0.2450	8.18	- 6.18
895-28	0.2350	9.03	- 5.99
896-40	0.2046	8.46	- 5.47
897-42	0.1915	7.71	- 7.04
897-12	0.1776	13.32	- 7.76
895-10	0.1566	7.34	- 5.05
897-10	0.1333	6.11	- 5.39
895A-5	0.1330	8.91	- 4.32
894-12	0.1131	5.74	- 2.54
895A-8	0.1046	3.88	- 2.20
895A-4	0.0917	8.83	- 2.99
895A-13	0.0603	4.17	- 1.02
897-53	0.0517	3.05	0.23
897-17	0.0283	7.34	0.40
896-26	0.0121	4.62	0.54
896-23	0.0064	3.14	0.72

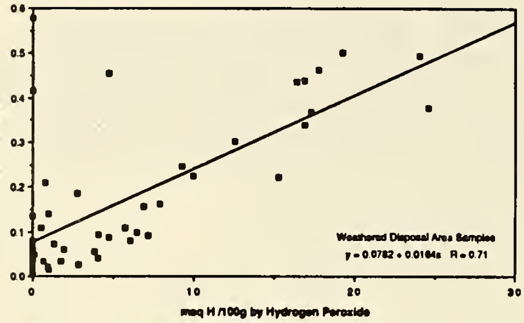

Figure 1a. Weathered disposal area samples.

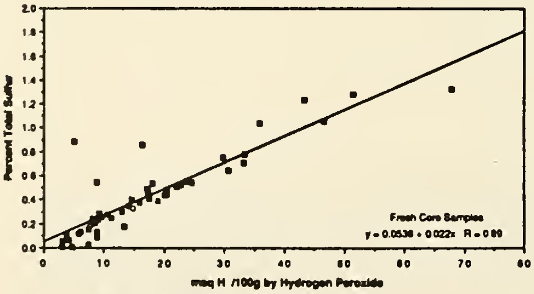

Figure 1b. Fresh core samples

Figures 1a-b. Comparison of total sulfur (auto analyzer) and potential acidity on weathered disposal area samples and fresh core samples on the divide section - Tennessee Tombigbee Waterway

Table--2. Total sulfur, milliequivalents of hydrogen by peroxide oxidation, and acid-base account of samples taken from overburden cores, Tennessee-Tombigbee Waterway.

Sample Number	Percent Sulfur	Meq H^+/ 100 G	Acid-Base Account $CaCo_3$ Equivalent Tons/1,000 Tons Material
1503-02	0.9203	52.34	-37.07
501-N1	0.5772	0.00	20.47
1504-P1L2	0.5013	19.23	-22.59
1503-L3	0.4926	24.06	-17.03
1504-K1	0.4633	17.78	-26.94
501-04#5	0.4554	4.76	-13.76
1504-K2	0.4386	16.91	-23.40
1203-02	0.4362	16.40	-19.25
501-J1	0.4153	0.00	203.92
1503-P1L5	0.3786	24.61	-13.21
1503-A2	0.3671	17.28	-19.31
1504-P1L4	0.3390	16.87	-11.05
1704-P1L3	0.3016	12.58	-14.12
1503-P2L4	0.2462	9.28	-11.84
1204-L3	0.2240	9.98	- 7.92
1503-P1L4	0.2218	15.27	- 8.31
1204-Q1	0.2111	0.82	1.06
1205-05#74	0.1863	2.74	-6.58
1704-P1L1	0.1629	7.92	-11.19
1203-L2	0.1582	6.86	-6.35
1508-04#34	0.1410	1.01	10.76
1503-05#45	0.1345	0.00	23.77
1204-02	0.1098	5.73	-2.36
1701-07#73	0.1091	0.52	14.45
1504-03#50	0.0999	6.47	-3.12
1503-F1	0.0943	4.13	-2.03
1203-F2	0.0920	7.18	-4.29
1504-H1	0.0869	4.76	-5.95
1504-R2	0.0803	6.08	-4.44
1203-F1	0.0797	0.00	24.27
1203-M1	0.0722	1.37	-1.56
1204-H1	0.0664	0.00	21.11
1203-01	0.0633	0.00	16.56
1204-I1	0.0597	1.99	0.57
1204-A2	0.0565	3.86	-1.92
1203-81	0.0503	0.00	14.86
1203-G1	0.0492	0.00	14.86
1203-E1	0.0474	0.16	2.74
501-C1	0.0411	4.03	-1.75
501-E1	0.0373	0.00	9.37
501-E2	0.0350	0.67	-0.86
501-E3	0.0337	1.76	-0.35
1204-SW	0.0318	0.00	3.14
1303-07#86	0.0289	0.00	19.35
1504-01	0.0262	2.81	-2.39
1504-I1	0.0210	0.94	-0.20
1501-05#82	0.0194	0.00	11.54
602A-04#2	0.0152	1.01	0.46
1304-SW	0.0102	0.00	1.47
1302A-02#25	0.0078	0.00	1.07

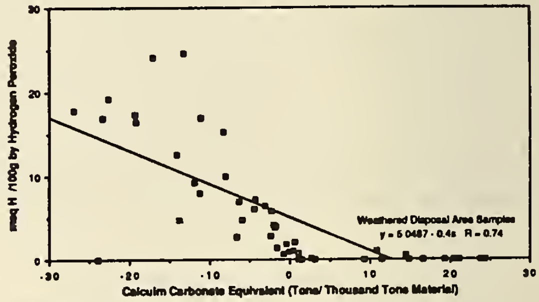

Figure 2a. Weathered disposal area samples.

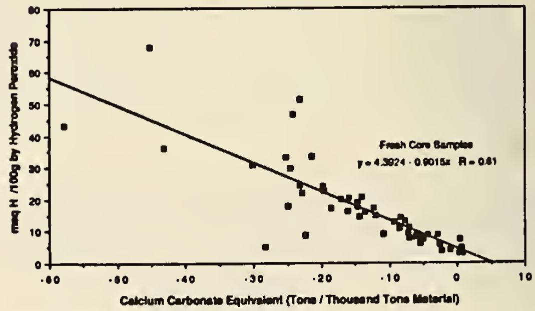

Figure 2b. Fresh core samples.

Figures 2a-b. Comparison of potential acidity and calcium carbonate equivalent on weathered disposal area samples and fresh core samples on the divide section - Tennessee Tombigbee Waterway.

Results from the comparison of the acid-base accounting on the fresh core samples are illustrated in figure 2b. There is high correlation between these methods ($r^2=0.81$). However, the same comparison on weathered disposal area soils shows a poor relationship between the two methods ($r^2=0.42$). Again, this suggests that weathering products may be interfering with the peroxide procedure.

CONCLUSIONS

A strong relationship exists between results obtained using peroxide oxidation and total sulfur by autoanalyzer for unweathered overburden core samples. This relationship was less pronounced on samples that have weathered following placement in disposal areas. Previous research has shown that in material that has been weathering for long periods of time, no relationship exists between the peroxide procedure and total sulfur by autoanalyzer (WVU 1971). When pyrite begins to weather in disturbed soil, various weathering products evolve. These weathering products interfer with the peroxide procedure for potential acidity in soil.

It was not within the scope of this study to examine the sources of error in the peroxide oxidation procedures; however, future research could be directed toward identification of the interfering compounds and development of methods to reduce or eliminate these interferences. Based on the peroxide procedure be limited to fresh, unweathered samples.

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THE INTERRELATION OF FACTORS INFLUENCING THE DISSOLUTION OF METALS IN COLUMNS OF MINE TAILINGS[1]

Richard D. Doepker[2]

Abstract.--The dissolution of metal species from silver mine mill tailings containing quartz (70%) and manganiferous siderite was investigated using a column leach procedure. The effects of leachant ionic strength, pH, and buffering ability were examined. The results indicated increased metal transport with increased ionic strength and decreased pH. In another test series, matched sets of columns were compared to determine the effect of leachate residence time on metal concentration. In these tests, leachate metal ion concentrations more than doubled in columns that were allowed to evaporate (wet/dry cycle) about 30% of their pore leachate volume. The pH of the leachate eluted from the dry cycle (unsaturated column) decreased while the conductance increased. Increases of five times were observed for lead and manganese, while increases of two orders of magnitude were seen for zinc and cadmium. The wet/dry cycle effect was enhanced during subsequent cycles, but appeared not to be influenced by the addition of sodium lauryl sulfate, sodium benzoate, or phenol, which are known to inhibit microorganism involvement. Increased sensitivity to further oxidation of those columns that underwent the dry cycle became apparent through increased deviation of the ion yields from duplicate columns. The interrelation of the above factors with the composition of the tailings present adds complexity to determining dissolution mechanisms.

INTRODUCTION

It is generally accepted that rain percolating through mine wastes can dissolve and transport metals through the wastes and into the surrounding area. Depending on the toxicity of the metals in question and their relative concentrations, such a situation could lead to contamination of surface and ground waters, rendering them toxic to plants, fish, and animals. The question is, therefore, how can it be determined whether an individual site contains hazardous material?

The methods presently used to predict acid mine drainage (Ferguson 1987), although not completely successful, do offer one factor that may well influence the concentrations of leached metal species, and that is acidity. Studies by Calspan (Brainbridge 1980) and A. D.

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Table 1.--Assay of silver mine tailings, pct.

Si	Fe	Al	C	Mn	Pb	Ca	Mg	S	Zn	K	Cu	As
35.4	6.6	2.4	1.8	0.65	0.43	0.25	0.25	0.16	0.11	0.08	0.04	0.02

Little, Inc. (Kuryk 1985), have produced additional information and protocols for column leach studies that may permit controlled laboratory experiments to intersect, divide, and isolate those kinetic and thermodynamic processes that influence the environmental mobilization of metal species through and out of mine mill tailings.

The laboratory program for this project involved a series of tests on mill tailings from a silver mine. We examined the effects of leachant ionic strength, leachant acidity, the presence of acetate ions, and the influence of a "wet and dry cycle" on the dissolution of metals. Analyses were performed on the leachates for aluminum (Al), calcium (Ca), cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), magnesium (Mg), nickel (Ni), potassium (K), sodium (Na), and zinc (Zn). Ionic conductivity and pH were also determined for each leachate. The purpose of the study was to isolate certain parameters and to determine their kinetic effects on the overall transport of metal species within the tailings sample.

MATERIALS AND METHODS

Waste

The silver mine tailings used in this investigation contained partially liberated quartz (70%) and manganiferous siderite ($FeCO_3$-Mn) as principal gangue minerals. The quartz and chert ranged from 10 to 15 micrometers and the siderite from 10 to 100 micrometers. The principal metallic minerals were pyrite (FeS_2), galena (PbS), sphalerite (ZnS), minor chalcopyrite ($CuFeS_2$), minor tetrahedrite [$(Cu,Fe,Zn,Ag)_{12}Sb_4S_{13}$], and minor muscovite [$KAl_3Si_3O_{10}(OH)_2$]. Particles of these minerals ranged from 1 to 20 micrometers in diameter. A trace of digenite (Cu_2S) and possibly arsenopyrite (FeAsS) were detected by X-ray diffraction. The pyrite was generally not attached to other minerals and had shiny unaltered surfaces even though the tailings were weathered. A few pyrite grains had inclusions of galena and chalcopyrite. About one-half of the galena was completely included within siderite or, rarely, quartz. Most of the remaining galena was attached to siderite grains but had exposed surfaces; only a minor portion of the galena was free. Sphalerite occurred as large unattached grains or smaller grains attached to siderite. Chalcopyrite and tetrahedrite most commonly occurred together as small inclusions in siderite or galena. A partial listing of the results of the destructive assay of the tailings is given in table 1.

The tailings samples used for all experiments were oven dried at 160° F in half-filled 55-gal drums. The material was crushed to its original size range, mixed well, and stored in large plastic drums.

Chemicals

All chemicals in this study were commercially available, analytical-grade reagents (A.R. grade) used without further purification. The deionized water was produced in the laboratory through distillation (Barnstead glass still) then deionized with a Barnstead NANOpure II Demineralizer[3] (18.8 megohm-cm). Leachant solutions were prepared by standard analytical techniques using only A.R. grade chemicals and prepared deionized water. They were then stored in carboys (Nalgene) until used.

Column Test Equipment and Methods

Leach columns were constructed from 2- or 4-ft lengths of 3-in-inside-diameter (ID) PVC pipe equipped with cemented couplings and bushings in which perforated Nalgene plates had been installed. A 9-cm G6 (Fisher Scientific) borosilicate glass fiber filter was placed on the perforated plate before installation of the bushing. Twenty of the 2-ft columns were mounted in a rack and arranged in groups of four, permitting a test sequence for five parameters. Combinations of other 2- and 4-ft columns were used for various specific experiments. A series of 10 similarly constructed 1-1/2-in-ID PVC columns were used to examine the effects of sample depth and column surface-to-volume ratios. These columns were arranged in series of two, again for a five-parameter study. Leachants were introduced to the columns drop by drop from a 1-liter polypropylene storage bottle through tygon tubing fitted with a screw clamp. Volumes of leachant used depended on an experimentally determined pore volume. Estimates of pore volume were made by weighing out 100 g of tailings, saturating the sample with deionized water, and placing it in a Buchner funnel. The sample was covered, allowed to drip-dry overnight, and then reweighed. The difference in weight represented the weight of water stored in the pores of the sample. The columns to be used in a test series were then filled with the appropriate weight of tailings and enough leachant to saturate the column plus an additional 150 cm^3. The difference between the leachant and leachate volumes gave a corrected pore volume. In all experiments, the leachant introduced was equal to or a specific fraction of the pore volume.

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[3] Reference to specific products or manufacturers does not imply endorsement by the Bureau of Mines.

Slurry Test Methods

Where slurry procedures were used, a weighed sample of the tailings was placed into a 500 cm^3 polypropylene rectangular bottle (Nalgene). Leachant was introduced in predetermined solid-to-liquid ratios. The bottles were placed on a variable-speed, reciprocating shaker for 4 to 16 hours. The samples were then filtered through no. 42 Whatman filter paper. The pH and conductivity of the leachate was determined, after which the leachate was acidified to $0.01\underline{M}$ nitric acid for analysis by atomic absorption techniques or to about 2% nitric acid for analysis with ICP.

Equipment

Most of the metal analyses reported in this investigation were carried out with the aid of an IL 551 atomic absorption spectrometer. With the acquisition of a Perkin-Elmer Plasma II, ICP became the method of choice for metal analyses.

DISCUSSION OF RESULTS

Ionic Strength Effect

Tables 2-A and 2-B report leachate concentrations for leachants of various ionic strengths and pH's. The experimental method utilized 3-in columns; 2 kg of tailings samples (10.5-11 in, depth) per each column; four replicates; five different leachants of $0.001\underline{M}$, $0.01\underline{M}$, and $0.10\underline{M}$ KNO_3; deionized water; and a sample of Western synthetic rain (Bainbridge 1980). The pore volume for this series was determined to be 500 cm^3. Leachant pH was adjusted to approximately 5.5 (table 2-A) or 2.0 (table 2-B) with nitric acid.

It should be noted that all species demonstrated a rapid decrease in concentration from that shown in the initial saturation experiment (test 84) when from two to three pore volumes of leachant were added. After this initial decrease, leachate concentrations reached a near-constant value for all species. In nearly all cases, the concentration of metal contaminants was greatest for the $0.10\underline{M}$ KNO_3 leachant. In general, the magnitude of this increased concentration was found to be due to changes in solubility as a result of changes in activity coefficients. Unfortunately, the increased leachate pH of nearly 0.4 was above similar expectations. Furthermore, it was expected that this increased leachate pH would decrease metal dissolution, resulting in a combined effect of little to no apparent change in ion concentration.

With the adjustment of the leachant pH to a value of 2.0 using nitric acid, metal dissolution increased while the solution maintained the previous ionic strength effect and the leachate pH decreased to a value between 4.1 and 4.5. This sample of silver mill tailings appeared to have a strong buffer region between a pH of 4.5 to 3.5. The pH of a 20:1 liquid:solid slurry formed with deionized water and the silver mill tailings when varying amounts of sulfuric acid were added reproduced this buffer region (fig. 1). Table 2-B shows that leachate concentrations for most metal species (tests 012 through 016) declined after the initial influence of the acidic leachant, and that repeated "washing" with deionized water returned the system to the pre-acid leaching condition. Nickel concentrations in the leachates were found to be below detection limits (0.06 ppm) until the pH 2 leachant was used. A value of 1.06 ppm was observed for nickel concentrations of $0.10\underline{M}$ KNO_3, 0.86 ppm for $0.01\underline{M}$ KNO_3, and 0.82 for $0.001\underline{M}$ KNO_3 (test 013). Initial cadmium leachate concentrations (test 84) were 0.39, 0.29, and 0.27 ppm for $0.10\underline{M}$, $0.01\underline{M}$, and $0.001\underline{M}$ KNO_3, respectively. These values decreased to below detection limits (0.01) for all leachant systems except the $0.10\underline{M}$ KNO_3 leachant (at 0.021) after the addition of two pore volumes of leachant (test 90). Cadmium concentrations remained below detection limits for all leachings until the acid leachant effect was observed, whereupon concentrations of 0.04 to 0.02 ppm were noted.

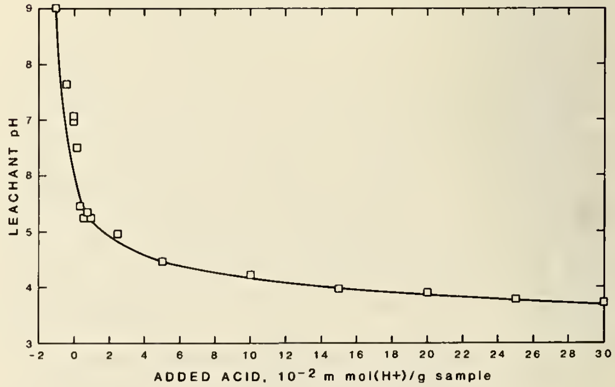

Figure 1.--Leachate pH as a function of added acid.

To further test the ionic strength effect, newly prepared columns containing 1.5 kg of the silver mill tailings were first leached with deionized water and then subjected to one of five leachants (0.10M KCl, 0.033M K_2SO_4, 0.10M KNO_3, 0.033M Na_2SO_4, or 0.10M $LiNO_3$) of identical ionic strengths. The results of the tests are summarized in table 3 and show that, in general, the ionic strength effect previously observed was independent of the salt used to control the ionic strength.

TABLE 2-A IONIC STRENGTH EFFECT

Ag-MINE TAILINGS 3-inch (i.d.) column; 2.00 kg in each; height ~10.5-11 inches.

AVERAGE (4 columns)

#	84	86	88	90	92	94	96	98	100	104	110	114
Resident time(hr)	start	72	96	48	48	48	96	96	48	288	48	288
Leachant volume	250	250	250	250	250	250	250	250	500	500	500	500
LEACHANT												
pH												
DW, pH = 5.40	6.90	7.07	7.23	7.41	7.36	7.34	7.44	7.61	7.44	7.47	7.52	7.66
0.001M,KNO3,pH=5.46	6.98	7.10	7.23	7.43	7.35	7.48	7.56	7.69	7.55	7.44	7.56	7.72
0.01M,KNO3,pH=5.43	6.94	7.12	7.23	7.26	7.29	7.50	7.60	7.75	7.71	7.72	7.76	7.86
0.10M,KNO3,pH=5.61	6.92	7.15	7.21	7.31	7.51	7.96	8.06	8.03	8.02	7.94	7.99	8.00
RAIN,(SYN),pH=4.50	6.96	7.12	7.25	7.38	7.38	7.54	7.60	7.67	7.48	7.50	7.60	7.66
Calcium (Ca), mg/L												
OW	590	627	598	95.9	29.7	22.6	25.3	22.4	17.0	22.6	16.9	19.5
0.001M,KNO3	630	668	606	97.5	28.9	23.6	26.3	22.7	16.4	22.3	18.2	21.6
0.01M,KNO3	680	774	623	91.3	33.5	26.5	28.7	24.2	17.9	23.9	21.5	22.8
0.10M,KNO3	982	958	406	48.4	39.5	32.8	34.2	31.5	20.2	31.1	21.0	28.4
RAIN,(SYN)	643	678	574	76.4	27.4	21.4	24.3	20.1	14.2	22.6	16.6	19.8
Conductance, mmho.												
DW, 0.0036 mmho	3.68	2.51	2.22	1.952	0.197	0.162	0.178	0.150	0.126	0.166	0.125	0.139
0.001M,KNO3, 0.156	3.70	2.56	2.31	0.648	0.302	0.289	0.311	0.288	0.265	0.312	0.257	0.274
0.01M,KNO3, 1.343	4.53	3.74	3.43	1.72	1.46	1.48	1.48	1.46	1.45	1.50	1.45	1.48
0.10M,KNO3, 11.54	13.2	13.2	11.7	10.7	11.0	11.5	11.7	11.6	11.6	11.7	11.8	11.8
RAIN,(SYN), 0.0144	3.59	2.59	2.16	0.434	0.186	0.156	0.174	0.146	0.123	0.164	0.122	0.138
Iron (Fe), mg/L												
DW	0.08	0.05	0.05	*	0.15	*	*	*	*	*	*	*
0.001M,KNO3	0.07	0.04	0.05	*	0.92	0.12	*	*	0.11	*	*	*
0.01M,KNO3	0.08	0.04	0.05	*	0.13	0.30	*	*	0.80	*	*	0.06
0.10M,KNO3	0.11	0.08	0.08	*	0.05	*	0.04	*	*	*	*	0.04
RAIN,(SYN)	0.08	0.07	0.04	0.04	0.04	*	*	*	*	0.04	*	*
* below dl, dl=0.04												
Magnesium (Mg), mg/L												
OW	145	12.7	2.72	2.86	2.44	2.28	2.90	2.23	1.99	3.21	1.97	2.50
0.001M,KNO3	150	11.8	3.27	2.44	2.55	2.45	2.85	2.09	2.02	2.80	1.90	2.38
0.01M,KNO3	148	13.7	6.62	4.32	3.49	2.88	3.36	2.37	2.39	3.07	2.44	2.64
0.10M,KNO3	144	16.8	13.13	5.01	3.85	3.30	4.20	3.15	2.88	4.75	2.68	2.80
RAIN,(SYN)	138	11.5	2.65	2.10	2.22	1.94	2.34	1.70	1.82	3.04	1.88	2.43
Lead (Pb), mg/L												
OW	3.38	2.26	1.50	0.49	0.34	0.31	0.24	0.18	0.16	0.24	0.17	0.17
0.001M,KNO3	3.34	2.42	1.64	0.49	0.39	0.34	0.27	0.24	0.13	0.26	0.17	0.25
0.01M,KNO3	3.60	2.55	1.67	0.63	0.51	0.42	0.33	0.29	0.17	0.25	0.14	0.24
0.10M,KNO3	6.88	4.07	1.90	2.90	0.67	0.52	0.41	0.26	0.20	0.28	0.17	0.21
RAIN,(SYN)	4.21	2.67	1.87	0.48	0.32	0.27	0.27	0.25	0.19	0.25	0.19	0.19
* below dl, dl=0.10												
Zinc (Zn), mg/L												
DW	21.3	7.35	3.48	0.638	0.218	0.164	0.160	0.138	0.109	0.185	0.150	0.267
0.001M,KNO3	20.3	9.51	3.59	0.636	0.254	0.201	0.197	0.157	0.114	0.284	0.193	0.325
0.01M,KNO3	22.9	9.56	4.89	1.31	0.679	0.440	0.294	0.226	0.174	0.242	0.195	0.328
0.10M,KNO3	33.1	15.4	8.33	2.58	1.00	0.506	0.292	0.240	0.193	0.277	0.235	0.440
RAIN,(SYN)	19.9	7.55	3.60	0.519	0.210	0.168	0.151	0.133	0.114	0.231	0.152	0.259

DW - deionized water

TABLE 2-B IONIC STRENGTH EFFECT
Ag-MINE TAILINGS 3-inch (i.d.) column; 2.00 kg in each; height ~10.5-11 inches.
AVERAGE (4 columns)

	008		010	012	013	014		016	018	019	021	022
Resident time(h	48		168	168	216	336		120	216	168	168	456
Leachant volume	500		500	500	500	500		500	500	500	500	500
LEACHANT		LEACHANT					LEACHANT					
pH		pH = 2.00										
OW	7.79	OW	7.65	4.65	4.17	4.35	DW	4.77	6.56	7.27	7.53	7.66
0.001M,KNO3	7.80	0.001M,KNO3	7.71	4.56	4.13	4.40	OW	4.81	6.91	7.48	7.65	7.69
0.01M,KNO3	7.99	0.01M,KNO3	7.84	4.71	4.21	4.39	OW	4.92	7.39	7.70	7.75	7.72
0.10M,KNO3	8.21	0.10M,KNO3	8.06	4.79	4.25	4.43	DW	5.04	7.92	7.90	7.85	7.82
RAIN,(SYN)	7.78	RAIN,(SYN)	7.64	4.72	4.15	4.30	DW	4.87	6.73	7.58	7.71	7.65
		LEACHANT					LEACHANT					
Ca, mg/L		pH = 2.00										
DW	16.6	OW	55.0	137	72.5	70.2	OW	36.4	10.2	13.7	14.2	24.7
0.001M,KNO3	17.7	0.001M,KNO3	47.5	137	74.0	55.2	DW	34.4	9.74	12.8	14.4	24.6
0.01M,KNO3	19.2	0.01M,KNO3	33.5	118	68.1	71.0	OW	36.8	11.2	13.6	15.4	25.9
0.10M,KNO3	20.4	0.10M,KNO3	28.2	103	76.0	64.6	OW	39.7	4.06	10.5	14.2	32.6
RAIN,(SYN)	16.7	RAIN,(SYN)	56.3	118	65.9	56.3	DW	31.7	7.93	11.7	13.8	23.7
		LEACHANT					LEACHANT					
Conductance,mmho		pH = 2.00										
DW	0.123	OW	0.421	2.11	2.18	nd	DW	1.97	0.125	0.105	0.113	0.165
0.001M,KNO3	0.261	0.001M,KNO3	0.471	2.21	2.27	nd	OW	2.00	0.147	0.116	0.119	0.169
0.01M,KNO3	1.47	0.01M,KNO3	1.79	3.38	3.40	nd	OW	2.98	0.282	0.150	0.139	0.183
0.10M,KNO3	11.9	0.10M,KNO3	12.3	13.5	13.5	nd	DW	11.9	0.714	0.234	0.162	0.262
RAIN,(SYN)	0.121	RAIN,(SYN)	0.433	2.10	2.22	nd	DW	1.96	0.129	0.108	0.113	0.162
		LEACHANT					LEACHANT					
Fe, mg/L		pH = 2.00										
OW	*	OW	*	219	336	337	OW	321	16.6	9.14	4.43	0.14
0.001M,KNO3	*	0.001M,KNO3	*	181	321	314	DW	330	12.9	5.39	3.93	0.18
0.01M,KNO3	*	0.01M,KNO3	*	195	325	290	OW	307	6.69	3.83	2.31	0.19
0.10M,KNO3	*	0.10M,KNO3	0.14	173	323	324	OW	310	0.88	1.29	1.42	*
RAIN,(SYN)	*	RAIN,(SYN)	0.05	203	354	354	DW	318	13.0	7.17	3.79	0.24
* below dl, dl=0.04		LEACHANT					LEACHANT					
Mg, mg/L		pH = 2.00										
OW	2.13	DW	6.06	44.3	22.4	24.8	OW	22.3	2.52	1.71	1.66	2.33
0.001M,KNO3	2.07	0.001M,KNO3	5.05	38.1	21.7	24.8	DW	19.6	2.26	1.63	1.60	2.48
0.01M,KNO3	2.40	0.01M,KNO3	3.80	47.9	22.4	26.4	DW	18.8	2.13	1.74	1.77	2.57
0.10M,KNO3	2.61	0.10M,KNO3	3.52	46.5	23.8	26.7	DW	19.0	0.77	0.95	1.17	3.06
RAIN,(SYN)	1.98	RAIN,(SYN)	7.54	58.5	22.3	23.6	DW	19.3	2.05	1.62	1.50	2.35
		LEACHANT					LEACHANT					
Pb. mg/L		pH = 2.00										
DW	0.13	DW	0.27	13.2	3.59	2.67	DW	0.41	0.20	*	*	*
0.001M,KNO3	0.12	0.001M,KNO3	0.40	8.63	4.16	2.37	DW	0.21	*	*	*	*
0.01M,KNO3	0.11	0.01M,KNO3	0.23	10.4	6.50	2.77	DW	1.36	*	*	*	*
0.10M,KNO3	0.16	0.10M,KNO3	0.18	8.65	1.65	0.33	DW	0.17	*	*	0.17	*
RAIN,(SYN)	0.15	RAIN,(SYN)	0.21	10.9	1.58	2.43	DW	0.20	0.11	*	*	*
* below dl, dl=.010		LEACHANT					LEACHANT					
Zn, mg/L		pH = 2.00										
DW	0.211	DW	0.886	15.0	19.2	32.7	DW	31.4	3.3	1.3	0.9	0.9
0.001M,KNO3	0.209	0.001M,KNO3	0.615	16.8	18.7	30.7	DW	31.4	2.9	1.1	0.9	0.9
0.01M,KNO3	0.249	0.01M,KNO3	0.416	22.4	20.3	39.9	DW	34.8	2.0	1.1	0.9	0.8
0.10M,KNO3	0.290	0.10M,KNO3	0.334	28.8	26.0	45.6	OW	38.8	0.5	0.7	0.8	0.8
RAIN,(SYN)	0.199	RAIN,(SYN)	0.787	17.7	18.5	35.8	DW	30.9	2.8	1.4	0.9	0.8

OW - deionized water

Residence Time, Wet/Dry Cycle Effect

Tables 2 and 3 indicate that the leachate ion concentrations appeared to be influenced by the residence time, that is, the time while the leachate remained in the column. A close inspection of these tables reveals that the concentrations of most species increased with increasing residence time, with the possible exception of lead (table 3) (test 055 compared to 063). In order to examine this effect further, the columns used in the "salt" study (table 3) were

TABLE 3 SALT EFFECT

Ag-MINE TAILINGS VIII 3-inch (i.d.) column; 1.50 kg in each; leachant volume, 350cc.

AVERAGE (4 columns)

#		032	035		037	042	045	049	055	059	063	068
Resident time(hr)		start	144		168	168	168	168	366	192	72	168
LEACHANT				LEACHANT								
pH												
	DW	6.47	6.49	0.10M,KCl,pH=5.49	7.24	7.30	7.61	7.73	7.87	7.93	7.96	7.97
	DW	6.53	6.25	0.033M,K2SO4,pH=5.59	7.28	7.43	7.82	7.95	8.15	8.08	8.15	8.10
	DW	6.28	6.96	0.10M,KNO3,pH=5.39	7.27	7.39	7.72	7.86	7.99	7.96	8.01	8.02
	DW	6.57	7.00	0.033M,Na2SO4,pH=5.63	7.57	7.46	7.79	7.91	8.06	8.07	n.d.	8.14
	DW	6.33	7.13	0.10M,LiNO3,pH=5.58	7.47	7.55	7.74	7.85	7.95	7.95	n.d.	7.98
--- n.d. not determined												
CALCIUM (Ca), mg/L												
	DW	655	277	0.10M, KCl	149	54.5	35.8	27.8	33.1	26.2	17.0	28.3
	DW	672	239	0.033M, K2SO4	98.8	64.4	35.7	26.9	35.9	28.5	20.8	34.7
	DW	656	239	0.10M, KNO3	123	60.2	33.6	25.3	27.5	25.5	17.7	31.1
	OW	635	231	0.033M, Na2SO4	80.4	65.5	30.6	27.1	33.1	31.8	26.1	25.3
	DW	687	178	0.10M, LiNO3	74.4	59.2	32.2	24.5	28.8	29.8	26.4	29.5
CONDUCTANCE, mmho												
	DW	2.72	1.04	0.10M,KCl,12.58mmho	2.16	12.27	12.92	13.17	13.26	12.76	13.13	13.04
	DW	2.73	0.99	0.033M,K2SO4,7.53mmho	1.18	7.35	7.84	8.39	8.09	7.76	7.91	8.00
	DW	2.74	1.04	0.10M,KNO3,11.80mmho	2.23	11.57	12.22	12.46	12.63	12.05	12.19	12.34
	DW	2.69	0.98	0.033M,Na2SO4,6.20mmho	1.24	6.25	6.55	7.13	6.81	6.49	n.d.	6.57
	DW	2.70	0.82	0.10M,LiNO3,8.95mmho	1.79	8.85	9.09	9.40	9.33	8.87	n.d.	8.95
--- n.d. not determined												
IRON (Fe), mg/L												
	DW	0.13	0.09	0.10M, KCl	0.14	0.17	0.09	0.06	0.08	0.05	0.10	0.16
	DW	0.12	0.07	0.033M, K2SO4	0.22	0.08	<.04	0.05	0.04	0.05	0.14	0.11
	DW	0.24	0.11	0.10M, KNO3	0.37	0.06	0.05	0.04	0.05	<.04	0.27	0.09
	DW	0.08	0.19	0.033M, Na2SO4	0.08	0.18	0.17	<.04	0.07	<.04	0.16	0.14
	DW	0.12	0.08	0.10M, LiNO3	0.11	0.25	0.15	0.08	0.07	0.08	0.14	0.22
MAGNESIUM (Mg), mg/L												
	DW	43.3	5.07	0.10M, KCl	12.2	5.77	3.02	3.00	4.41	3.28	2.57	3.29
	DW	41.0	4.98	0.033m, K2SO4	11.3	6.19	2.64	2.80	4.28	3.77	2.78	3.58
	DW	43.7	4.81	0.10M, KNO3	12.3	5.63	2.96	2.86	3.91	3.28	2.72	3.21
	DW	41.6	5.01	0.033M, Na2SO4	7.64	6.13	2.49	2.37	3.33	3.38	3.14	3.50
	DW	40.3	4.26	0.10M, LiNO3	7.44	5.67	2.46	2.60	3.09	2.88	3.15	5.16
LEAD (Pb), mg/L												
	DW	2.86	1.14	0.10M, KCl	0.64	0.76	0.37	0.28	0.30	0.20	2.45	0.34
	DW	3.12	0.66	0.033M, K2SO4	0.63	0.69	0.34	0.23	0.29	0.24	1.27	1.30
	DW	2.93	0.78	0.10M, KNO3	0.61	0.43	0.43	0.34	0.24	0.14	10.7	0.48
	DW	2.94	1.20	0.033M, Na2SO4	0.42	0.44	0.20	0.29	0.25	0.26	0.23	1.08
	DW	3.38	0.82	0.10M, LiNO3	0.39	0.34	0.33	0.26	0.26	0.19	3.68	n.d.
--- n.d. not determined												
ZINC (Zn), mg/L												
	DW	12.8	2.50	0.10M, KCl	1.55	1.52	0.61	0.44	0.84	0.76	0.58	0.55
	DW	13.4	1.75	0.033M, K2SO4	1.07	1.12	0.58	0.42	0.69	0.64	0.45	0.42
	DW	13.3	1.89	0.10M, KNO3	1.57	1.20	0.41	0.37	0.52	0.44	0.32	0.42
	DW	13.8	2.57	0.033M, Na2SO4	0.76	0.77	0.63	0.52	0.75	0.42	0.33	0.59
	DW	13.4	2.29	0.10M, LiNO3	1.12	0.92	0.51	0.41	0.45	0.40	0.27	0.40

OW - deionized water

divided into pairs, two of which were maintained at near-saturation conditions while the other was allowed to dry partially. The averages of the two saturated (even-numbered) and unsaturated (odd-numbered) columns before and after the wet/dry cycle are presented in table 4. It becomes apparent that those columns allowed to evaporate approximately 30% to 40% of their pore liquid produced an environment that resulted in increased metal dissolution and decreased leachate pH. After stabilization (addition of three pore volumes of "salt" leachant), the process was repeated. The results were similar. Presumably, this was because of atmospheric oxidation of the sulfide minerals present in the unsaturated zone and the subsequent formation of acid (Nordstrom et al. 1979, Nordstrom 1982). In order to examine a possible relation between microorganism activity and oxidation, sodium lauryl sulfate, sodium benzoate, or phenol (Watzlaf 1986) were added to three sets of columns, while 0.01$\underline{M}$ KNO_3 and 0.01$\underline{M}$ KNO_2 leachants were used on the remaining two sets. Although the presence or absence of microorganisms was not experimentally established, it was assumed that the treatment should have eliminated them from contributing to the next wet/dry cycle experiment. It may be noted that this test (test 104) produced effects

TABLE 4-A. SAT./UNSAT. EFFECT

Ag-MINE TAILINGS 3-inch (i.d.) column; 1.50 kg in each; leachant volume, 350 cc

AVERAGE (2 columns)

#		059	068		073	075	080	083	088		095	104	108
Resident time(hr)		192	168		504	168	168	504	168		336	576	120
					SAT/UNSAT			SAT/UNSAT				SAT/UNSAT	
AVG.	LEACHANT			AVG.					LEACHANT	LEACHANT			LEACHANT
pH	KCl								DW(ALL)	SLS			DW(ALL)
2&4	(0.10M)	7.92	7.98	SAT.	7.91	8.00	8.07	8.03	8.05	550mg/L	7.88	7.89	7.74
1&3	pH=5.49	7.94	7.97	UNSAT.	7.25	7.81	7.96	7.31	7.72	pH=5.40	7.78	7.32	7.70
	K2SO4									NaBz			
6&8	(0.033M)	8.09	8.11	SAT.	8.09	8.15	8.17	8.12	8.21	578mg/L	8.00	8.10	7.91
5&7	pH=5.59	8.06	8.09	UNSAT.	7.80	8.01	8.07	7.55	7.96	pH=6.13	7.92	7.18	7.74
	KNO3									KNO3			
10&12	(0.10M)	7.90	8.03	SAT.	8.09	7.89	8.07	7.98	8.02	0.01M	7.82	7.97	8.01
9&11	pH=5.39	8.02	8.01	UNSAT.	7.51	7.85	8.00	6.92	7.82	pH=5.40	7.71	5.00	6.99
	Na2SO4									PHENOL			
14&16	(0.033M)	8.11	8.15	SAT.	8.06	8.13	8.18	8.16	8.30	578mg/L	7.82	8.00	7.97
13&15	pH=5.63	8.04	8.13	UNSAT.	6.95	7.87	8.19	7.38	8.03	pH=5.10	8.02	7.97	8.04
	LiNO3									NaNO2			
18&20	(0.10M)	7.94	8.00	SAT.	7.98	7.89	8.07	7.93	8.06	0.01M	7.95	7.96	7.97
17&19	pH=5.58	7.95	7.97	UNSAT.	7.55	7.82	7.98	7.18	7.94	pH=6.06	7.74	5.66	7.20
CALCIUM (Ca), mg/L													
2&4	KCl	27.80	29.30	SAT.	20.30	26.95	21.15	23.80	18.10	SLS	1.31	1.53	0.89
1&3	(0.10M)	24.70	27.40	UNSAT.	53.75	28.30	21.85	112.25	27.20	550mg/L	6.55	47.9	10.9
6&8	K2SO4	28.50	38.00	SAT.	23.05	31.35	24.00	29.20	18.45	NaBz	2.53	4.18	4.98
5&7	(0.033M)	29.60	31.50	UNSAT.	47.60	27.90	23.05	68.30	18.20	578mg/L	2.75	59.5	12.9
10&12	KNO3	25.90	35.90	SAT.	17.95	22.60	16.35	24.30	14.90	KNO3	13.0	17.2	10.5
9&11	(0.10M)	25.20	26.30	UNSAT.	50.30	23.80	18.40	81.75	15.15	0.01M	18.8	101	18.6
14&16	Na2SO4	33.30	24.70	SAT.	21.30	32.05	22.45	26.55	23.80	PHENOL	12.0	14.6	13.6
13&15	(0.033M)	30.30	26.00	UNSAT.	96.75	37.85	31.85	232	52.70	578mg/L	17.1	81.3	30.7
18&20	LiNO3	29.30	31.60	SAT.	21.30	37.60	24.60	31.20	22.95	KNO2	11.8	15.7	12.3
17&19	(0.10M)	30.30	27.40	UNSAT.	56.10	21.40	27.50	90.75	18.00	0.01M	20.7	82.9	15.4
MAGNESIUM (Mg), mg/L													
2&4	KCl	3.43	3.30	SAT.	3.16	3.84	2.71	1.30	2.26	SLS	0.15	0.27	0.11
1&3	(0.10M)	3.14	3.27	UNSAT.	10.2	4.02	4.12	11.9	2.90	550mg/L	0.75	7.02	1.63
6&8	K2SO4	3.70	3.84	SAT.	3.21	4.30	3.29	2.08	2.54	NaBz	0.25	0.50	0.42
5&7	(0.033M)	3.85	3.32	UNSAT.	8.62	3.74	3.94	8.15	2.36	578mg/L	0.28	7.33	1.77
10&12	KNO3	3.33	3.28	SAT.	3.64	3.38	2.69	1.45	2.08	KNO3	0.92	1.70	1.27
9&11	(0.10M)	3.23	3.15	UNSAT.	8.82	3.59	3.30	8.48	1.87	0.01M	1.82	14.9	3.01
14&16	Na2SO4	3.29	3.53	SAT.	2.60	4.59	3.33	1.33	6.26	PHENOL	1.15	1.34	1.14
13&15	(0.033M)	3.46	3.47	UNSAT.	14.5	5.07	4.57	26.4	4.06	578mg/L	3.12	10.7	3.92
18&20	LiNO3	2.99	5.90	SAT.	2.43	4.33	3.30	1.38	2.68	NaNO2	1.24	1.71	1.61
17&19	(0.10M0	2.72	4.43	UNSAT.	7.98	3.63	4.91	7.85	2.15	0.01M	2.03	11.9	2.36

DW - deionized water

TABLE 4-B SAT./UNSAT. EFFECT.

Ag-MINE TAILINGS, 3-inch (i.d.) column; 1.50 kg in each; leachant volume, 350cc.

AVERAGE (2,columns)

#		059	068		073	075	080	083	088		095	104	108
Resident time(hr)		192	168		504	168	168	504	168		336	576	120
					SAT/UNSAT		SAT/UNSAT					SAT/UNSAT	
AVG.	LEACHANT			AVG.					LEACHANT	LEACHANT			LEACHANT
CONDUCTANCE	KCl								DW(ALL)	SLS			DW(ALL)
2&4	(0.10M)	12.76	13.04	SAT.	10.79	13.02	13.42	12.72	11.68	550mg/L	0.429	0.393	0.275
1&3	12.58mmh	12.75	13.01	UNSAT.	15.54	13.53	13.66	16.55	10.85	0.165mmho	0.521	0.835	0.330
	K2SO4									NaBz			
6&8	(0.033M)	7.78	8.03	SAT.	6.60	8.07	8.59	8.89	6.94	578mg/L	0.567	0.519	0.432
5&7	7.53mmho	7.74	7.98	UNSAT.	8.92	8.60	8.89	10.60	6.94	0.363mmho	0.590	1.105	0.510
	KNO3									KNO3			
10&12	(0.10M)	12.14	12.56	SAT.	9.76	11.89	10.60	12.23	10.94	0.01M	1.635	1.715	1.411
9&11	11.88mmh	11.97	12.12	UNSAT.	14.25	12.97	13.31	15.61	10.40	1.507mmho	1.720	2.850	1.434
	Na2SO4									PHENOL			
14&16	(0.033M)	6.45	6.56	SAT.	5.52	6.74	7.11	6.72	5.87	578mg/L	0.106	0.135	0.112
13&15	6.20mmho	6.54	6.58	UNSAT.	7.67	6.96	6.67	9.46	5.85	0.059mmho	0.222	0.546	0.243
	LiNO3									NaNO2			
18&20	(0.10M)	8.88	8.97	SAT.	7.81	9.04	0.00	8.92	8.07	0.01M	1.420	1.476	1.261
17&19	8.95mmho	8.86	8.94	UNSAT.	10.93	9.41	9.78	11.69	7.38	1.301mmho	1.465	2.335	1.209
LEAD (Pb), mg/L													
2&4	KCl	0.22	0.28	SAT.	0.11	0.22	0.12	0.32	0.14	SLS	<.1	<.1	<.1
1&3	(0.10M)	0.18	0.39	UNSAT.	10.66	0.69	0.21	1.71	0.43	550mg/L	0.14	0.51	0.17
6&8	K2SO4	0.24	1.31	SAT.	0.13	0.25	0.13	0.16	0.12	NaBz	0.09	<.1	<.1
5&7	(0.033M)	0.24	1.30	UNSAT.	0.48	0.43	0.19	1.39	0.42	578mg/L	0.16	0.55	0.37
10&12	KNO3	0.14	0.53	SAT.	<.1	0.15	<.1	0.11	2.37	KNO3	0.07	<.1	0.10
9&11	(0.10M)	0.14	0.43	UNSAT.	0.35	0.32	<.1	1.38	0.23	0.01M	0.11	5.46	1.88
14&16	Na2SO4	0.24	0.86	SAT.	0.17	0.24	0.12	0.19	0.24	PHENOL	0.14	0.10	0.11
13&15	(0.033M)	0.27	1.30	UNSAT.	3.01	0.64	0.18	2.05	0.24	578mg/L	0.10	0.10	0.14
18&20	LiNO3	0.20	n.d.	SAT.	0.20	0.29	<.1	0.14	<.1	KNO2	0.25	0.10	0.11
17&19	(0.10M)	0.19	n.d.	UNSAT.	5.14	0.45	0.20	2.20	0.60	0.01M	0.25	7.51	1.95
ZINC (Zn), mg/L													
2&4	KCl	0.95	0.75	SAT.	0.56	0.53	0.42	0.63	0.34	SLS	0.08	0.39	0.25
1&3	(0.10M)	0.56	0.35	UNSAT.	5.32	0.96	0.83	12.3	2.60	550mg/L	0.31	3.60	0.86
6&8	K2SO4	0.54	0.40	SAT.	0.28	0.27	0.22	0.31	0.15	NaBz	0.05	0.10	0.08
5&7	(0.033M)	0.75	0.43	UNSAT.	1.43	0.84	0.66	4.86	1.01	578mg/L	0.18	5.35	1.95
10&12	KNO3	0.50	0.44	SAT.	0.31	0.40	0.31	0.45	0.27	KNO3	0.28	0.41	0.19
9&11	(0.10M)	0.39	0.40	UNSAT.	1.86	0.78	0.60	7.20	1.13	0.01M	0.51	15.4	5.97
14&16	Na2SO4	0.44	0.33	SAT.	0.22	0.23	0.16	0.25	3.65	PHENOL	0.11	0.12	0.06
13&15	(0.10M)	0.39	0.85	UNSAT.	24.1	2.07	0.82	42.3	1.33	578mg/L	0.61	0.59	0.50
18&20	LiNO3	0.39	0.37	SAT.	0.39	0.57	0.30	0.63	0.36	KNO2	0.18	0.20	0.24
17&19	(0.10M)	0.42	0.44	UNSAT.	1.73	0.79	0.70	11.8	1.62	0.01M	0.98	17.1	3.79

DW - deionized water

very similar to those observed prior to treatment, which would indicate that the effects of microorganisms were minimal and that atmospheric oxidation was primarily responsible for increased leachate contamination. It should be pointed out, however, that somewhat greater pH decreases were observed for the untreated samples than had been previously seen.

Both nickel and cadmium were below detection limits (nickel = 0.06, cadmium = 0.01) prior to the first wet/dry cycle. Concentrations of nickel ranged from 0.55 (with a Na_2SO_4 leachant) to 0.12 ppm (with $LiNO_3$) for unsaturated columns while ranges below detection (using Na_2SO_4) to 0.08 ppm (using KCl) were observed for those columns that remained saturated. Similar results were also seen for cadmium, except values ranged from 0.26 (Na_2SO_4) to 0.024 ppm (KNO_3) for unsaturated columns. All saturated columns recorded concentrations below detection.

Acetate Ion Effect

At the present time, acetic acid buffers are used to control the pH of a specific leachate. The EP toxicity and the TCLP (U.S. EPA 1985) slurry tests are two examples where acetic acid is used. There have also been suggestions involving the mixing of mine tailings with other organic matter as a prelude to growing a vegetation cover. Since acetate ions are known to complex with certain metal species (for example, lead), a series of tests were conducted to examine the effects of acetate ions on the dissolution of metal from the silver mill tailings. The results of the initial series tests are given in table 5. Here, five sets of four columns each were leached with leachants of 0.10$\underline{M}$ NaOAc, pH = 6.03; 0.01$\underline{M}$ NaOAc, pH = 6.02; 0.001$\underline{M}$ NaOAc, pH = 6.04; 0.10$\underline{M}$ KNO_3, pH = 5.79-control; and 0.10$\underline{M}$ NaOAc, pH = 6.97 to establish the influence of acetate ions.

All species reported in table 5 demonstrate increasing metal concentrations with increasing acetate concentrations. Furthermore, the metal ion concentrations of 0.10$\underline{M}$ acetate, pH = 6.03, were greater than those of 0.10$\underline{M}$ KNO_3, pH = 5.79. This would indicate that acetate complex formation does increase the dissolution of metals within this sample of tailings. However, one major difficulty remains, i.e., the presence of potassium nitrate elevates the leachate pH above that of the acetate leachate even though the leachant pH is lower for the potassium nitrate solution. It should also be noted that the metal ion concentrations obtained for the acetate buffer at pH = 6.97 are somewhat greater than those of the potassium nitrate control even though the resulting leachate pH is greater for the acetate buffer. These results would seem to indicate that the presence of acetate ions will increase the dissolution of metals from mine wastes.

SUMMARY AND CONCLUSIONS

Although limited to the tailings from a single mine, the results of this study indicate an ionic strength effect on the dissolution of contaminants from mine tailings. This effect may be partially explained through the standard secondary salt effect (effect on species activity coefficients) through ion exchange between the leachant and the tailings. Thus, treatments of tailings with materials that produce high ionic strength leachate may well enhance the dissolution of specific components in the wastes. It would also appear that the chemical nature of the inorganic ion within the range of an ionic strength of 0.1$\underline{M}$ has very little effect on the concentration of metal species leached from the tailings.

It appears that this sample, which is a low-pyrite, high-siderite sample, will undergo destructive oxidation resulting in decreased leachate pH and increased metal dissolution. This oxidation originates in the unsaturated zone and does not appear to involve microorganisms.

The presence of acetate ions has a pronounced effect on the dissolution of metals from mine waste samples. Increased solubility of magnesium, manganese, and lead would be expected through the formation of acetate complexes. The dissolution of other species, such as zinc, nickel, and cadmium, also appears to be increased in the presence of acetate ions. Care must be exercised regarding actions that could lead to acetate production in the proximity of mine tailings.

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TABLE 5. ACETATE ION EFFECT

Ag-MINE TAILINGS 3-inch (i.d.) column; 1.50 kg in each; leachant volume, 350cc.

AVERAGE (4 columns)		#	110	115	117	119		3-01	3-05
		Resident time(hr)	144	192	168	168		168	168
		LEACHANT					LEACHANT		
pH	PRIOR	0.10M,KNO3,pH=5.79	7.86	7.72	7.95	8.05	DW	8.18	8.37
	LEACHANT	0.10M,OAc,pH=6.03	7.11	7.55	7.61	7.53	DW	7.63	8.20
	(DW)	0.01M,OAc,pH=6.02	7.82	7.78	7.94	7.77	DW	8.05	8.09
		0.001M,OAC,pH=6.04	7.92	7.91	7.94	7.41	DW	7.90	7.87
		0.10M,OAc,pH=6.97	7.63	7.91	8.20	8.30	DW	8.38	8.52
CALCIUM (Ca) mg/L	PRIOR	0.10M,KNO3,pH=5.79	46.2	34.7	21.2	20.4	DW	15.6	1.05
	LEACHANT	0.10M,OAc,pH=6.03	60.3	83.4	65.4	69.6	DW	54.60	4.60
	(DW)	0.01M,OAc,pH=6.02	16.2	21.3	11.8	12.6	DW	10.3	2.50
		0.001M,OAc,pH=6.04	19.5	14.8	13.1	13.2	DW	12.0	11.9
		0.10M,OAc,pH=6.97	60.3	30.3	15.2	14.0	DW	12.8	0.70
MAGNESIUM (Mg) mg/L	PRIOR	0.10M,KNO3,pH=5.79	7.52	3.49	2.27	2.23	DW	1.70	<0.05
	LEACHANT	0.10M,OAc,pH=6.03	10.2	6.80	6.40	7.15	DW	5.80	0.43
	(DW)	0.01M,OAc,pH=6.02	1.79	1.97	1.27	1.20	DW	1.05	0.15
		0.001M,OAc,pH=6.04	2.70	1.80	1.72	1.63	DW	1.50	1.45
		0.10M,OAc,pH=6.97	13.2	3.58	1.77	1.53	DW	1.53	<0.05
MANGANESE (Mn) mg/L	PRIOR	0.10M,KNO3,pH=5.79	11.3	8.89	2.92	2.22	DW	1.55	0.04
	LEACHANT	0.10M,OAc,pH=6.03	18.3	26.8	14.8	13.0	DW	9.43	0.69
	(DW)	0.01M,OAc,pH=6.02	2.92	2.71	1.62	1.68	DW	1.31	0.36
		0.001M,OAc,pH=6.04	2.09	1.53	1.20	1.25	DW	1.06	1.28
		0.10M,OAc,pH=6.97	7.40	4.77	2.17	2.55	DW	2.62	0.04
NICKEL (Ni) mg/L	PRIOR	0.10M,KNO3,pH=5.79	0.12	0.08	0.01	0.03	DW	0.01	<.005
	LEACHANT	0.10M,OAc,pH=6.03	0.17	0.20	0.20	0.25	DW	0.22	0.01
	(DW)	0.01M,OAc,pH=6.02	0.03	0.02	<.005	0.01	DW	0.01	<.005
		0.001M,OAc,pH=6.04	0.04	0.02	0.01	0.02	DW	0.01	0.02
		0.10M,OAC,pH=6.97	0.06	0.02	<.005	0.02	DW	0.01	<.005
LEAD (Pb) mg/L	PRIOR	0.10M,KNO3,pH=5.79	0.28	0.23	0.07	0.36	DW	<.03	<.03
	LEACHANT	0.10M,OAc,pH=6.03	2.94	6.94	3.40	5.09	DW	1.17	0.11
	(DW)	0.01M,OAc,pH=6.02	0.18	0.19	0.08	0.19	DW	0.06	0.03
		0.001M,OAc,pH=6.04	0.11	0.08	0.04	0.45	DW	<.03	0.03
		0.10M,OAc,pH=6.97	1.59	1.44	0.58	0.57	DW	0.40	<.03
ZINC (Zn) mg/L	PRIOR	0.10M,KNO3,pH=5.79	3.74	2.25	0.92	0.91	DW	0.46	0.02
	LEACHANT	0.10M,OAc,pH=6.03	3.91	4.08	5.60	10.42	DW	6.80	0.52
	(DW)	0.01M,OAc,pH=6.02	0.95	0.77	0.52	0.55	DW	0.37	0.12
		0.001M,OAc,pH=6.04	0.40	0.26	0.24	0.26	DW	0.20	0.23
		0.10M,OAc,pH=6.97	2.99	1.36	0.76	0.86	DW	0.72	0.03

DW - deionized water

IMPROVED ROCK DURABILITY TESTING TECHNIQUES FOR APPALACHIAN VALLEY FILLS[1]

Robert A. Welsh, Jr. and Michael K. Robinson[2]

Abstract.--The integrity and stability of gravity-placed or end-dumped excess spoil fills in the Appalachians is partially dependent upon placement of durable rock material. Standard durability tests do not adequately discriminate between nondurable and durable rock. Review of recent rock durability research has identified testing procedures and classification systems that may be more applicable to excess spoil fills and the surface mining process. A geotechnical testing program, incorporating the transfer of this recent technology, has been designed by the U.S. Office of Surface Mining Reclamation and Enforcement to allow better prediction of rock durability for a range of overburden materials. An array of rapid, inexpensive rock competency tests are being compared to determine which tests or combination of tests give correlative results which allow accurate prediction of rock durability. Preliminary results from 18 rock samples collected from minesites in Kentucky, Virginia, and West Virginia suggest that tests which measure rock swelling upon water immersion are particularly valuable in predicting the behavior of marginally durable shales. Simple swell tests, when combined with rock strength tests, seem to provide the most efficient discrimination between rocks of similar appearance, but widely varying durability. An additional 84 rock samples collected from 43 minesites in Virginia, West Virginia, Kentucky, and Tennessee are being analyzed to further refine the testing techniques and to investigate the primary mechanisms contributing to slaking.

INTRODUCTION

Excess spoil consists of overburden (soil and rock excavated during the mining operation) not needed to reclaim the disturbed area to the approximate original contour. Before the Surface Mining and Reclamation Act of 1977 (SMCRA), excess spoil structures were constructed with minimal engineering guidance.

Often these structures were placed at locations selected strictly to optimize mining operations. Little thought was given to potential environmental consequences or safety hazards. Since the passage of SMCRA, there has been an increase in the engineering effort directed toward design and construction of excess spoil disposal areas.

In general, methods of placement for excess spoil include: (a) the lift type construction method; (b) the head-of-hollow fill method; and (c) the durable rock (gravity) fill method.

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In the lift method, excess spoil is usually deposited in uniform, horizontal lifts of 4 ft or less and compacted to achieve the desired density. Prior to placement of the spoil in this type of fill, the foundation must be prepared and underdrains installed. According to U.S. Office of Surface Mining Reclamation and Enforcement (OSMRE) regulations at 30 CFR Section 817.71(f)(3), the rock comprising the underdrain must be durable (rock that will not slake in water nor degrade to soil material); non-acid or toxic forming; and free of coal, clay or other non-durable material.

An alternative method for excess spoil disposal involves the placement of spoil in lifts at the upper reaches of a watershed. This "head-of-hollow fill" method originated in West Virginia in the early 1970's, and combines the lift-placement technique and a durable rock chimney drain in the center of the fill. The "rock core chimney drain" results from physical segregation of larger rock during spreading of spoil material and lift compaction. All surface and subsurface drainage is to be controlled by this rock core, in order to prevent elevation of the phreatic surface within the fill mass. This type of fill must be placed where the surface drainage entering the core is minimized to prevent a decrease in permeability due to clogging of the rock core by fine particles.

The durable rock fill method consists of dumping spoil to its angle of repose into valleys in a single high lift or several smaller lifts. In existing fills, the lifts range between 50 to over 400 ft in thickness. The front face of the fill is then graded to develop a terraced fill configuration. The material forming the rock fill is generally made up of angular blast rock. According to 30 CFR Section 816.73, the durable rock fill method can only be used if durable rock overburden is present and comprises at least 80 percent by unit volume of the fill. No designed underdrain is required for this type of fill, in as much as the gravity segregation which occurs upon dumping forms a highly permeable zone of large-sized durable rock in the lower one-third of the fill.

The successful performance of excess spoil structures is directly related to the durability of the rock in the fill mass and underdrains. As D.R. Casagrande noted in a public hearing on OSMRE proposed rules concerning spoil in fills:

> "Spoil materials range from hard rocks to clay shales and even soft clay. The range of engineering properties of such materials is enormous. Therefore the proposed rules must be sufficiently conservative to also include the properties of the weakest materials." (Casagrande, 1978).

Durable rock is defined in Federal regulations at 30 CFR Section 816.73(b) as rock which does not slake in water and will not degrade to soil material. A rule-of-thumb used by regulatory authorities is that durable rock achieve an as-tested slake durability index (I_D) of at least 90. The intent of the durability standard is to selectively obtain rock that can withstand surface mining conditions including blasting, handling, compaction, and weathering without significant degradation. The key concern is that, over the long term, a durable rock fill should behave more as a rock mass than as a soil mass. A rock mass is inherently more stable than a soil mass of similar volume because rock has much greater load-carrying capacity and resistance to movement or consolidation than soil. Durable rock fill material has this greater strength because of high intergranular friction and greater resistance to shear stress. Nondurable rock will degrade into soil-sized particles as a result of overburden pressure and moisture absorption, and the drainage system provided by the void space between the rocks may become clogged. The clogging may cause excess pore water pressures to develop that will cause a decrease in the shear strength of the fill material. This decrease in shear strength can cause the failure of the excess spoil structure. Therefore, the correct assessment of the durability of the rock is a critical design factor.

The OSMRE recognizes the need for a suitable rock durability standard. The objective is to select a rapid, inexpensive durability testing standard which will clearly differentiate between durable and nondurable materials, model the effects of surface mining conditions on rock materials, and allow assurance of the long-term stability of properly designed fill structures.

Durability classification systems that involve more than two tests may be uneconomical and are subject to the accumulative effect of mechanical and human errors during testing. Franklin (1970) and Bieniawski (1974) consider the following as necessary prerequisites for any rock classification system employed on a routine basis:

1. System should be based on measurable parameters determinable by relevant tests performed quickly and inexpensively in the field;

2. System should involve only rapid testing techniques due to the potential for large numbers of routine samples;

3. Testing techniques should be simple enough to be carried out by semiskilled field and laboratory staff; and,

4. The range of test result values should allow for a sufficient power of discrimination when applied to the various test samples.

MATERIALS AND METHODS

Samples

The rock samples tested in this study were collected from recently blasted highwalls of surface mines in Kentucky, Virginia, and West Virginia. Eighteen grab samples of freshly blasted rock weighing approximately 100 lb were collected at each site. To facilitate coring during laboratory sample preparation, large, competent blocks of rock were selected. Detailed descriptions of geologic properties and minesite conditions relating to rock durability were made on site, and photographs were taken of the sampled highwall. A dilute hydrochloric acid effervescence (fizz) test for calcareous cementing agents was performed for each sample.

Early to Middle Pennsylvania-age sandstones, shales, and mudstones were sampled for this study. These include overburden and interburden rocks of the Hazard and Peach Orchard Coal zones of the Breathitt Formation in Kentucky; Standiford, Taggart Marker, and Low Splint Coal zones of the Wise Formation in Virginia; and, Freeport and Kittanning Coal zones of the Allegheny Formation, and the Coalburg Coal zone of the Kanawha Formation in West Virginia.

Rock analyses

Geologic materials removed from their in situ environment during the surface mining of coal exhibit changes in physical integrity. Such changes are caused by physical and chemical mechanisms induced by variations in moisture and stress regimes. The rock in fills has been subjected to blasting, handling, compaction, and weathering. Generally speaking, a sedimentary rock that can withstand these processes without significant changes in its original structure can be classified as a durable rock.

When selecting durable rock for fills, one should choose a single test or a combination of tests that best simulate surface mining conditions (Robinson and Ventura 1983). For this study, recent research on rock durability has been reviewed, and testing techniques were selected for application to surface mining rock fills. In order to establish which test or combination of tests best serves as an indicator of sedimentary rock durability, a laboratory testing program was designed to simulate the moisture changes and stress regimes that a sedimentary rock undergoes during the processes of excavation and placement in excess spoil fills. After conducting a wide variety of tests, including Modified Los Angeles Abrasion tests, Modified Slake Durability Index tests, and US Army Corps of Engineers (COE) Accelerated Weathering tests, among others, a simplified testing protocol evolved.

The program presently includes the following tests:

a) Slake Durability Testing, which is currently accepted by OSMRE, includes minor abrasion effects and saturation-desiccation stresses. As defined by Chandra (1970) and Franklin and Chandra (1972), oven-dried samples of rock are placed in a wire mesh drum partially immersed in water. The drum is rotated at 20 rpm for approximately 10 minutes; the sample is then removed, dried, and run through a second cycle.

b) Uniaxial Unconfined Compressive Strength Tests simulate loading stresses in a fill. They are run on rock cores loaded in the direction normal to bedding. Loading is applied to the point of breakage, defined as the maximum stress; constant loading rate of 8,000 lb/min was used.

c) Atterberg Limits Testing is an indicator of the type of clay minerals in the rock and their plasticity. This involves measuring the liquid limit, plastic limit, and plasticity index of the fine grained (minus #40 sieve size) fraction of the rock material.

d) Swell Testing indicates the slaking stress that affects rock when it is removed from its in situ environment in the overburden. This is done by measuring the volume expansion of the cored rock normal to bedding upon immersion in water for a period of 24 hours after oven drying to 105 degrees C. A dial gage is used to measure any dilatancy. Swelling strains are probably the result of expansion due to air breakage along interconnected voids such as microcracks in the rock (Olivier 1979).

e) Jar Slake (Soak) Tests were run to provide a qualitative measure of rock behavior after immersion in water for a 24-hour period. The sample is immersed in a beaker, and observations of any disaggregation are made. As Andrews et al. (1980) state, "...this test might be most closely related to spoil materials located at depth and within a constant humidity or totally saturated environment."; therefore these tests are particularly relevant to the durability of underdrain rock in valley fills.

The above tests were conducted by the COE Ohio River Division Geotechnical Engineering Laboratory under the testing protocol designed by OSMRE. In this discussion, test results for only a limited number of sedimentary rock samples are reported. Thus, any conclusions presented herein should be considered as preliminary until results are available for a wider range of samples currently being tested.

RESULTS AND DISCUSSION

Data from the laboratory testing program are listed in tables 1 and 2. The values obtained in the laboratory for parameters including the swelling strain, slake durability index, unconfined

Table 1.--Atterberg limits data and Deere and Gamble (1971) plasticity classifications for sampled Appalachian shales.

Sample Number	Liquid Limit (%)	Plastic Limit (%)	Plasticity Index (%)	Plasticity Rating
RR-1	30	21	9	Low
CB-3	33	22	11	Medium
KS-1	30	22	8	Low
KS-2	32	22	10	Low/Medium
AR-1	28	21	7	Low
AR-2	35	27	8	Low
WR-2	36	26	10	Low/Medium
IF-3	35	24	11	Medium
RR-1a	37	22	15	Medium

Table 2.--Swelling coefficients, compressive strengths, slake durability indices, and Franklin and Chandra (1972) and Olivier (1979) classifications for Appalachian rock samples.

Sample Number	Rock Type	Swelling Ratio (DL/L)	Compressive Strength (lb/in^2)	Slake Durability Index (%)	Durability Classification: Franklin/ Chandra (1972)	Durability Classification: Olivier (1979)
RR-1	Shale	0.0085	11,880	98.5	V.high	M.poor
CB-3	Shale	0.0486	930	94.8	M.high	V.poor
KS-1	Shale	0.0125	2,850	97.2	High	V.poor
KS-2	Mudstone	0.0299	2,210	94.9	M.high	V.poor
AR-1	Shale	0.0020	3,060	95.9	High	M.poor
AR-2	Shale	0.0146	1,670	96.4	High	V.poor
WR-2	Mudstone	0.0142	- -	29.6	V. low	V.poor
IF-3	Shale	0.0280	180	92.1	M.high	V.poor
RR-1a	Shale	0.0010	3,080	95.9	High	Fair
RR-2	Sandstone	- -	14,280	98.3	V.high	Excellent
CB-1	Sandstone	0.0018	6,670	92.5	M.high	Excellent
CB-2	Sandstone	- -	6,050	84.0	Medium	Excellent
KS-1a	Sandstone	0.0004	3,480	95.7	High	Excellent
PH-1	Sandstone	0.0002	4,200	89.1	M.high	Excellent
AR-3	Sandstone	0.0003	6,630	97.9	High	Excellent
WR-1	Sandstone	- -	5,060	96.8	High	Excellent
IF-1	Sandstone	0.0008	5,150	94.3	M.high	Good
CB-1a	Sandstone	0.0006	3,660	96.7	High	Good

- - indicates value too low for accurate measurement.
M. = moderately.
V. = very.
DL/L = ratio of change in sample length to original sample length.

uniaxial compressive strength, and Atterberg limits of the rocks, wherever applicable, were used to classify their durability under the classification systems developed by Franklin and Chandra (1972), Deere and Gamble (1971), and Olivier (1979). None of the rock samples had significant calcareous cement, based on negative fizz test results.

Durability classification of the sampled rock is shown graphically in figures 1 through 3, using single and multiple index classification systems. The single index classification system developed by Franklin and Chandra (1972) uses only the slake durability index test data to assess durability. Slake durability of the rock is assessed by an index, I_D, defined as the percentage retention measured by dry weight after two cycles of testing (fig. 1). This test was adopted by OSMRE as the accepted standard, and thus has been widely used among the coal industry for the selection of durable rock. Figure 1 indicates that, for the rocks sampled in this study, the slake durability test lacks sufficient discrimination to reveal durability differences between sedimentary rocks as disparate as sandstone, shale, and mudstone. Furthermore, the overwhelming majority of sampled rocks are uniformly ranked as highly durable. Several authors have also reported similar problems in the use of the slake durability index as applied to geotechnical projects such as highway or tunnel construction (Duncan et al. 1968, Noble 1977, Olivier 1979, Richardson 1985). Published difficulties with the test include:

1. During testing, some of the more plastic shales may form mudballs, thus rendering falsely high I_D values (Richardson 1985).

2. The test does not differentiate very well between shales (Noble 1977).

3. The test is insensitive to shales which slake into small chips which are larger than the #10 sieve (2 mm) size of the openings in the hardware cloth forming the testing drums (Duncan et al. 1968, Olivier 1979). This effect was duplicated in shale samples tested in the present study, where high I_Ds of over 90 were attained, yet the shale samples disintegrated into masses of small chips in the soak test (fig. 4). Breakdown of rock into such small soil-like particles in fills may lead to soil-like behavior under the large load factors developed in the fill mass, and fill failure may result.

Additional concerns specific to surface mining were raised by Welsh et al. (1985):

1. The test fails to subject rock samples to the types of physical stresses common to surface mining conditions (impact, heavy abrasion, saturation and desiccation, compaction, etc.).

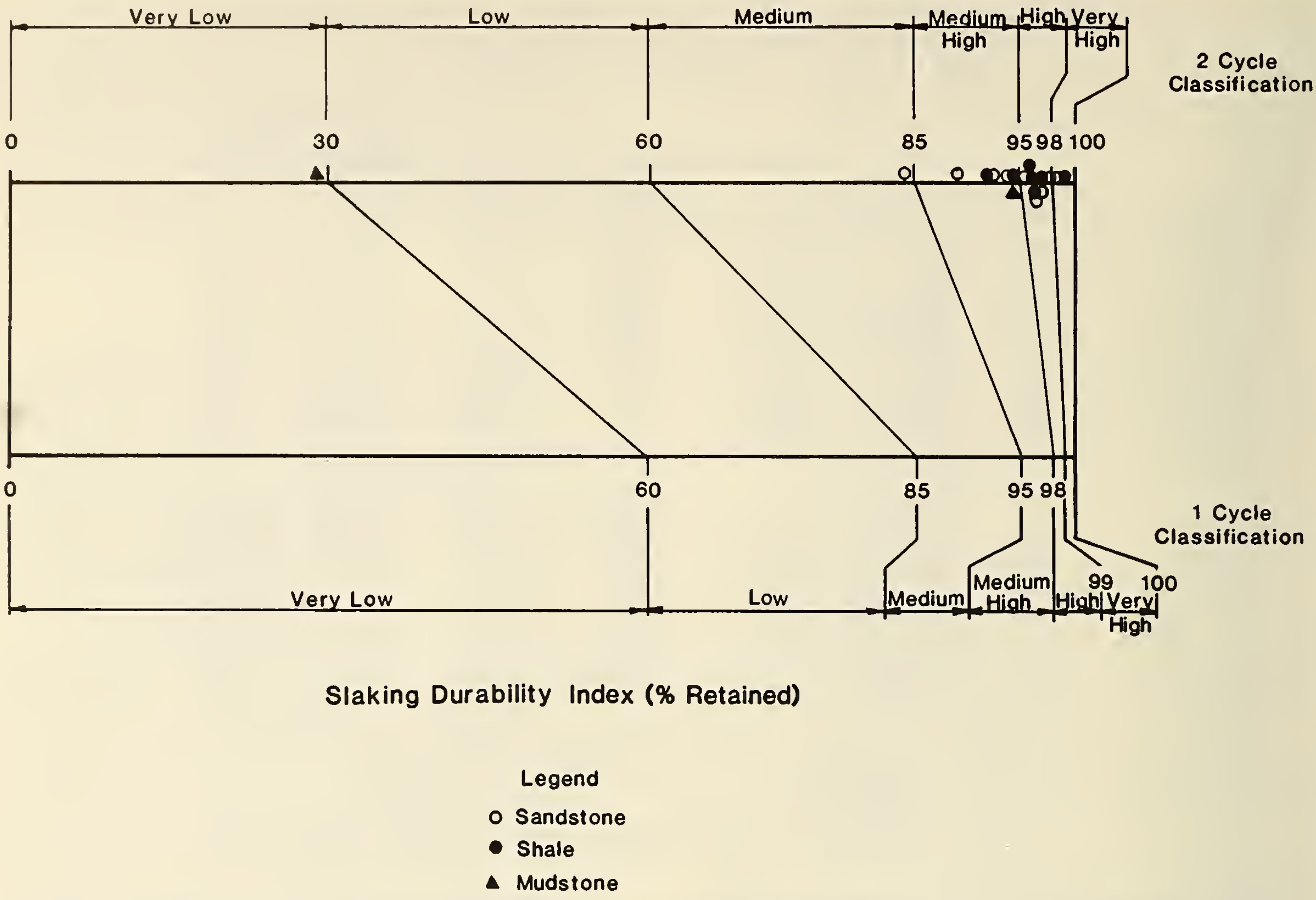


Figure 1.--Classification of Appalachian rock samples under the Slake Durability Index System of Franklin and Chandra (1972).

2. The index does not assess properties of rock samples indicative of rock-like or soil-like behavior.

3. Samples classified as durable in the laboratory exhibit soil-like behavior in the mining process.

Recognizing these problems in using the slake durability test exclusively as a single index measure of rock durability, other classification systems incorporating additional geotechnical tests were compared to the slake durability test standard. Dual-index graphical classification systems developed by Deere and Gamble (1971) and Olivier (1979) were utilized to provide a basis for correlation of durability measures.

The Deere and Gamble (1971) durability classification system is based on the two-cycle slaking durability and the plasticity index of sedimentary rocks. The data from the present study indicate a slightly better resolution between shale, mudstone, and sandstone durability as classified under the Deere and Gamble (1971) system, compared to slake durability testing alone (fig. 2). Sandstones, since they exhibit negligible plasticity, plot at the base of the chart; while shales and mudstones are distributed across the chart by their plasticity values. Gamble (1971) and Deere and Gamble (1971) found from laboratory testing that the plasticity of sedimentary rocks is inversely related to their slake durability. Therefore, higher plasticity values would decrease the rock durability. However, the Deere and Gamble (1971) system makes no attempt to adjust slake durability test rankings based on plasticity values. This classification system suffers from the same problems as the Franklin and Chandra (1972) test because it incorporates slake durability test data.

Olivier (1979) and Duncan (1969) recorded sedimentary rock behavior when it is removed from the in situ environment. Rocks swell and disintegrate as a result of stress relief. This swelling increases as rock absorbs moisture. Olivier (1979), also found that as swelling increases, the uniaxial compressive strength of the rock decreases. The resulting rock durability classification system involves the measurement of two rock properties. The first parameter is the magnitude of rock swelling after a dried sample is immersed in water. The second is the uniaxial compressive strength. Broad categories of "geodurability" ranging from very poor to excellent were assigned by Olivier (1979) based on ratios of compressive strength to swelling coefficient.

Classification of the rocks sampled in the present study using the Olivier (1979) system shows good discrimination between rock types and even between rocks of the same type (fig. 3).

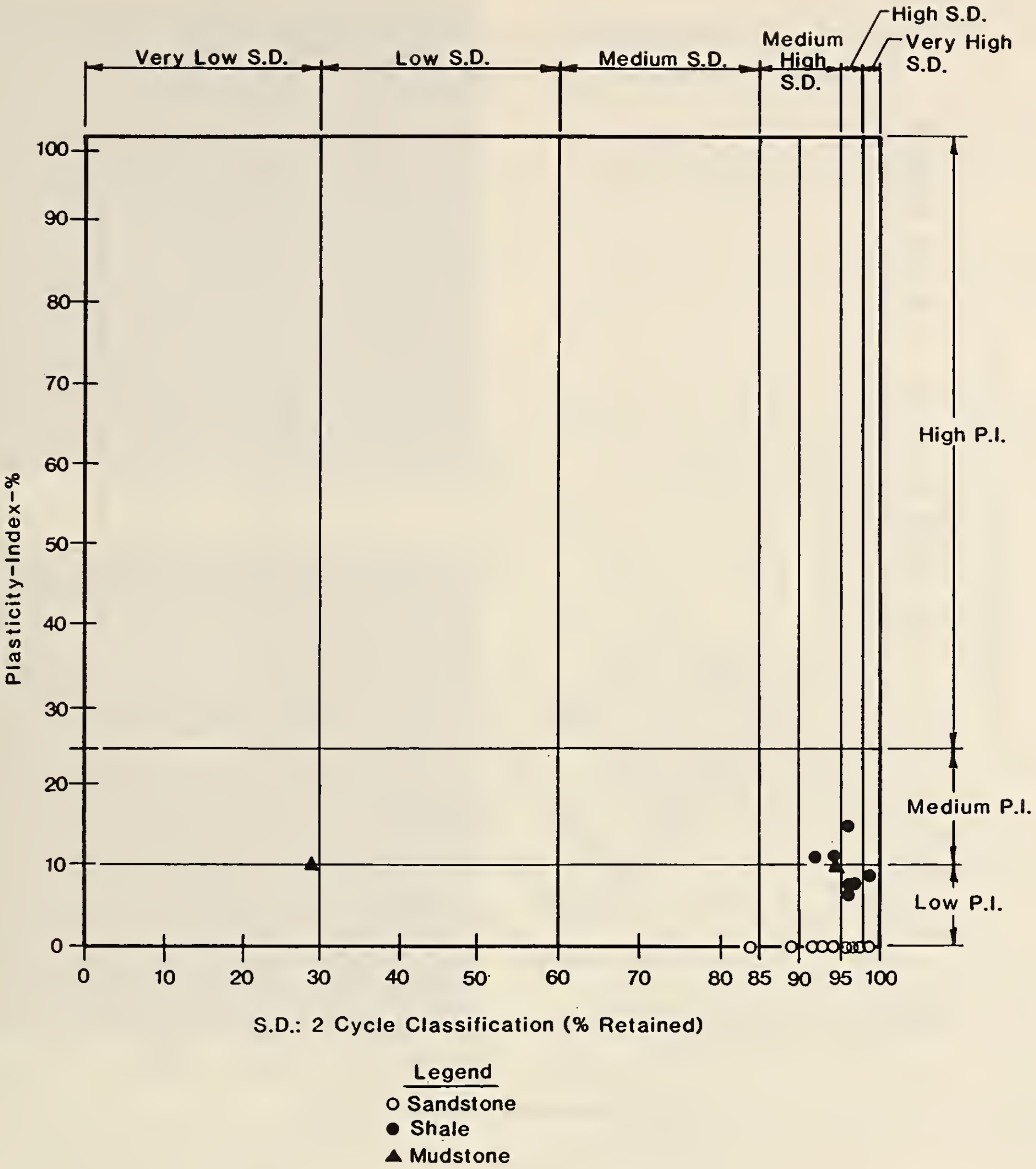


Figure 2.--Classification of Appalachian samples under the Deere and Gamble (1971) System.

Sandstones plotted in the good to excellent geodurability class, while shales ranged from fair to very poor. Mudstones ranked as very poor. The shales plotted into two subpopulations, grouped as moderately poor-fair, and very poor. Such results, if substantiated by further testing of a variety of rock, could be used to distinguish between tougher, more durable shales, and shales and mudstones which should be considered as nondurable.

Results from the soak tests support the Olivier geodurability assessments. Shales with slake durability indices of at least 90 (high durability) were rated as poor in geodurability, and disaggregated into fine, soil-like particles in the soak test (fig. 4). Therefore it appears that for the samples tested, the slake durability testing was not rigorous enough to accurately assess rock durability.

SUMMARY AND CONCLUSIONS

Comparison of the three classification systems indicates that all the systems correlated well in classifying the sampled sandstones as rocks with generally high durability. For shale and mudstone durability, however, the classification systems varied in usefulness. The Franklin and Chandra (1972) slake durability index and the Deere and Gamble (1971) classification system did not effectively distinguish between rock types of different durability. The reliance of these classification systems on the slake durability index test, which has inherent problems identified earlier, is the reason for this failure.

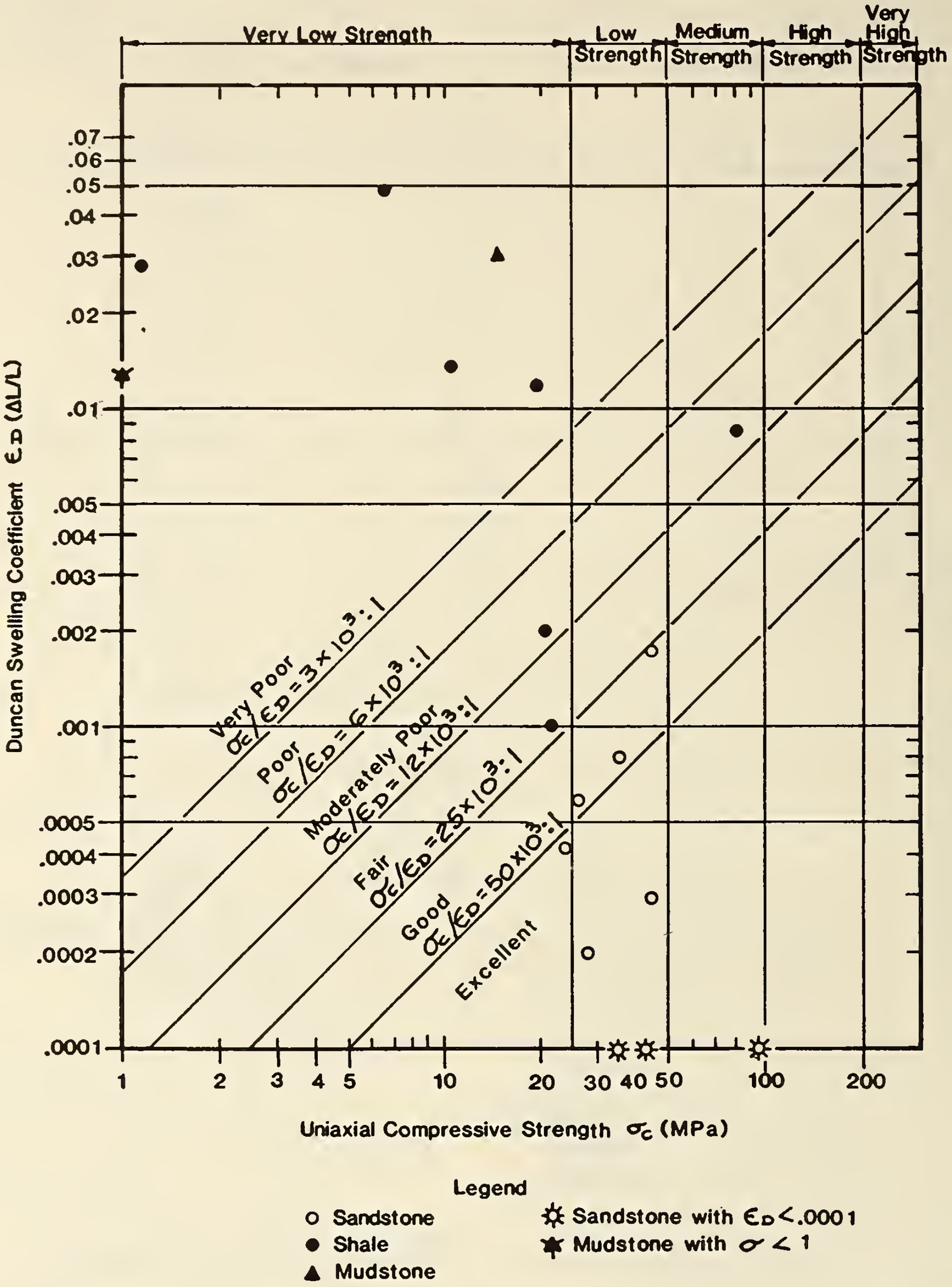
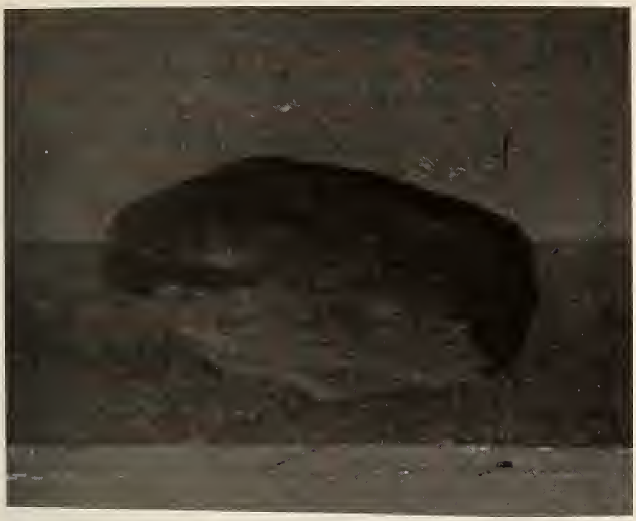


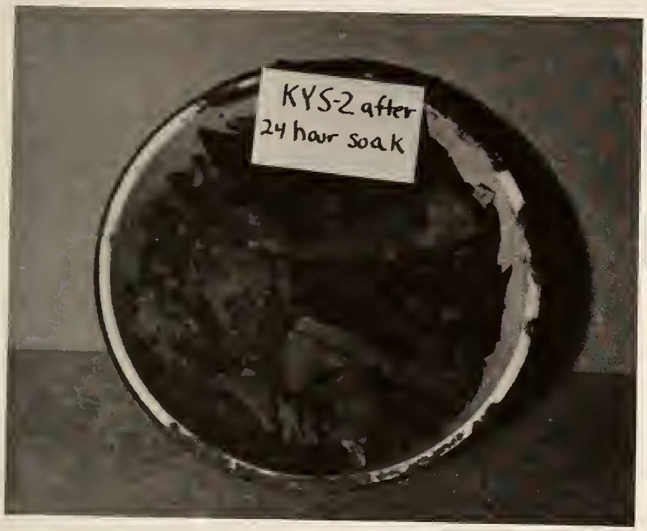
Figure 3.--Classification of Appalachian rock samples under the Olivier (1979) Geodurability System.

The Olivier (1979) classification system shows promise as a more accurate measure of rock durability, particularly for rock materials of marginal durability, such as shale. Correlation with soak test results indicates that the swell and compressive strength tests measure factors which are pertinent to the original concerns regarding rock durability in surface mining valley fills.

Further testing will be performed at COE laboratories to assess the reproducibility of results utilizing a testing protocol including swell, compressive strength, and soak tests on 84 additional rock samples from 43 minesites in Kentucky, Tennessee, Virginia, and West Virginia, and to compare these assessments with those from the slake durability index test. Point load testing results will be compared to uniaxial compressive strength testing, for possible interchangability of these rock strength tests. The geodurability rankings in the Olivier (1979) system will be modified to reflect experience gained through the testing of Appalachian rock material to better assess the durability of rock placed in excess spoil fills.



Sample K S-2 before Soak Test.



Sample K S-2 after 24-hour Soak.

Figure 4.--Qualitative soak test result for Appalachian shale sample.

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ACID MINE DRAINAGE RESEARCH: HYDROLOGY'S CRITICAL ROLE AND UNIFYING THEME

Frank T. Caruccio[1]

Abstract.--With some exceptions, in innovative treatment techniques many of the concepts and theories regarding acid mine drainage were postulated over 35 years ago. And much of the mine drainage related research currently performed should be integrated by a unifying concept and directed toward the solution of a principal objective - namely, the in-situ abatement of acid mine drainage. A central element which can provide a vehicle for unifying research directed toward this end and which is least understood and studied, is the hydrology of a backfill. A discussion is presented to justify soliciting proposals directed primarily toward and better understanding of the nature, occurrence and movement of water within spoil/backfill material.

Knowledge of the occurrence, distribution and description of water movement in a backfill, collectively defined by the hydrology, is critical to an understanding of the chemical evolution of water as it recharges the backfill and eventually emerges as a seep. The quality of the seep produced determines whether or not a bond is released, impacts the overall economics of the mining operation and affects the permitting decisions of future mines in that area. To date, few studies have addressed the hydrology of backfilled sites, primarily, I suspect, because of the difficulty of obtaining a hydrologic data base that requires drilling of the backfill material and properly installed wells and piezometers. Other than the ground water installations required to monitor quality, there is little incentive to drill costly monitoring wells in a backfill. Of the mine drainage issues, the hydrology of the system, although the most important part of the problem, remains the biggest unknown. If there is little incentive to drill and thoroughly explore an acid producing reclaimed site to determine what went wrong, imagine the incentive to hydrologically explore a non-acid site to find out what was done right! Let's look first at the acid side of the issue.

From an historical perspective, acid mine drainage has been a persistent problem, plaguing and limiting coal development as a viable energy base. Although simple to explain, the problem has yet to be solved on a level whereby regulatory agencies may feel comfortable in granting permits to mine certain seams in certain areas. Indeed, during the last 30 years substantial progress has been made in the prediction methodology, understanding the nature of the problem and in treatment technology (particularly in reclamation of landscapes and treatment of acidic mine drainages). Yet, in those problem areas, acid waters continue to be produced and although recent mine plans are designed to minimize or contain underground the acid loads, the mining and reclamation strategy necessary to completely eliminate acid mine drainage continues to elude us.

Further, the cost of treating and controlling acid mine drainage has been estimated to be in excess of 5 billion dollars (1970 dollars)- one wonders how this entire scenario can be economically viable! The severance taxes and reclamation funds instituted by the Mining Act, that are currently being returned to the states, are beneficial but the reclamation efforts are usually directed toward alleviating mine related problems which remotely address acid water abatement. More often than not, considerable efforts are directed toward the revegetation of an abandoned mine site, with peripheral attempts toward water quality amelioration; in all fairness probably due to a lack of a demonstrated effective in-situ treatment rather than intent.

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During my 25 years or so in acid mine drainage research I initially directed my efforts toward an understanding and prediction of acid mine water. Over the last ten years my efforts have been directed toward the mitigation of acid waters through the in-situ manipulation of the hydrology and geochemistry of infiltrating or recharge waters. As part of this overall effort, several ancillary studies developed with regard to prediction technology and the hydrology of a backfill. And over the past 15 years or so, through several committee appointments, I was able to periodically review the state of the art of acid mine drainage research, nationally as well as internationally. Based on what you are familiar with, consider the following concepts and their applications to the abatement of acid mine drainage:

1. The acidity of acid mine drainage originates not from free acid but from the hydrolysis of certain iron sulfates (by products of pyrite oxidation).

2. The occurrence of the problem is geographically limited to certain parts of the bituminous coal field.

3. Concentrations of acidity vary with conditions of flow to produce variations in loads.

4. The primary source of acidity is pyrite or marcasite in the roof shales, binders and rider seams.

5. Acid formation is associated with the concurrent growth of iron-oxidizing bacteria and the bacteria serve as catalysts.

6. The key factors in the formation of acid mine drainage are the presence of finely divided pyrite which is exposed to the atmosphere and the oxidation of ferrous by bacteria.

7. The problem is related to the occurrence of sulfates of iron, aluminum and manganese.

Further, recommended research on control programs might be aimed at: (a) the control of the disposition of the iron sulfides, (b) prevention of contact of iron disulfide with air and water,(c) reduction of bacterial activity and (d) removal of the objectionable impurities from acid mine water.

Sound familiar? ALL of the above were gleaned from literature dated no recent than 1954! The classic works of S.A. Braley, L.V. Carpenter, R.L. Starkey, K.L. Temple and W.A. Koehler, to name a few, and my apologies to the other giants in the field who were not mentioned, go back to the early 1930's in publication dates. Other than the few major breakthroughs, primarily in treatment, what is the stage of our progress to date and since then, how have the overall research efforts been structured to build upon these concepts and observations reported over 35 years ago?

A review of the recent literature in acid mine drainage research shows that little has been added to the basic pool of knowledge central to the mitigation of acid formation at the pyrite site. Several breakthroughs have occurred in the treatment technology, notably, the wetlands treatment of acid waters, the surfactant bactericides developed to control the iron oxidizing bacterial activity and the large scale treatment facilities designed to handle large volumes of acidic water. However, how much closer are we toward solving the problem? It seems to me that the acid mine drainage problem which in itself is overwhelming, has been dissected into minute parcels of research, for funding expediency and/or clarity of thought, which have been taken independently away from the central objective related toward the solution of the problem. Today, with some notable exceptions, very little research is integrated into a unifying conceptual theme. Commonly, the results are reported to answer the objectives of the study and little is done to take the data and conclusions from that realm into the real world through the synthesis of ideas or integration into the other facets of the acid mine drainage problem. For example, the worth or value of a study that shows a chemical aspect of the acid problem would be greatly enhanced if the results of the study can be integrated into the hydrology of the site and further developed toward field application. Unfortunately, the research has been so finely refined that the trees become identified as not being part of the forest.

As a first step toward addressing the solution of the acid mine drainage problem through a perpetual and effective in-situ abatement technique let me suggest that future research in acid mine drainage abatement studies be structured to interrelate two or more aspects of the natural system and restrict funding to those projects that can demonstrate that the final results can be easily integrated into an ever expanding data base. The pyramid concept should be introduced with the keystone being the solution to the problem and supporting research constituting the building stones and blocks that establish the base, but at the same time converge toward the central objective. It seems that today we continue to lay a broader and broader base with no sense of convergence occurring within the immediate future.

In soliciting proposals, funding agencies commonly call for studies within extremely broad categories the are related to the problem, but which do not provide convergence or direction toward addressing a central objective. Consider the RFP published in the September 18, 1987 Commerce Business Daily, soliciting research proposals "... to provide practical solutions to selected problems of abandoned coal mines. Proposed research must result in the development of innovative technologies, have wide regional application and be completed in a short time frame." The request then goes on to say that they are particularly interested in the areas of "...water quality, specifically abatement of acid mine drainage from a) underground mines, and b) refuse piles..."

Understandably the request is structured in the broadest description to encourage novel, innovative and unique approaches that may not as yet been conceptualized. I agree with this strategy. But at the same time could not part of the solicitation be line item specific, calling for directed research leading toward a specified objective. This may invoke a response from an expertise or talent, though not familiar with the overall problem of acid mine drainage, who may become involved in the research through directed efforts. For example, one of the key elements in the problem being discussed is the occurrence of water within a refuse pile or backfill and the critical role that it plays in the mass transfer and production of acidity and alkalinity. How is water recharged to the spoil, what is the distribution of the pores, what rock type generates the greatest porosity and provides the greatest alkaline/acid potential, what is the residence time of the water recharging the spoil, and how are the discharges controlled at the toe or outflow to produce seeps? Are the seeps an admixture of multi-channel flows or large reservoir bleeds? Each of these is a major unknown and must be addressed. In addition to the solicitation described above could not these research needs be specifically identified and targeted for proposals? A master plan must be organized that contains a convergence of studies and research efforts directed toward the solution of the problem.

I am a firm believer in the value of basic research. Certainly, it is through this avenue that data bases are developed, which, in turn, are synthesized into hypotheses and become foundations for applied and pragmatic research. But, realistically, how much closer are we toward solving the problem than we were twenty five years ago. Over the years, and especially within the last ten years, a substantial amount of time, effort and money has been spent on the acid mine drainage problem. From my perspective, the data and conceptual base has been expanded, tremendously. Developments in predictive technology have provided insight into the nature and character of sulfide reactivity, reclamation efforts have provided insight into the mature of the pore gases and their evolution giving us a better understanding of the hydrogeochemistry of the problem. Treatment technology advances have given us a variety of mitigative applications that may or may not be site specific, but certainly are restricted to specific settings within the backfill or spoil pile (i.e. in order to be effective, phosphate amendments must be juxtaposed to reactive sulfide sites-consequently are limited in application to active or reconstructed sites). And numerous studies characterizing the physical aspects and geometries of the problem sites have yielded broad insights into the chemistry, hydrology and biology of the problem. The time has come to reexamine the broad base of completed studies that are laterally distributed and to recognize a common element upon which the vertical development and integration of the results can proceed and upon which a strategy for directed research can be developed..

If the principal objective addresses mine drainage quality then it appears logical to link the studies by a water related concept and, as a unifying theme, integrated by interpreting the results of the study within the vehicle of the hydrologic cycle. Consider the pathways of a drop of water as it enters the cycle as precipitation. And, depending upon the time of the year and the intensity and duration of the event, it will either run off and reflect the quality of the precipitation and surface chemistry, penetrate the near surface and reflect the quality of an actively leached horizon, or recharge deep within the backfill and reflect a quality of deep interior reactive spoil. Within each profile the variations in the degree of saturation and pore gas composition greatly affect the kinetics of alkalinity and acidity formation. Further, the physical character of the litho type, coupled with the method of mining, will control the pathway of water movement within the spoil (i.e., bouldery material will provide enhanced porosity and permeability, whereas clayey, friable material will inhibit water flow) and, in turn, the chemistry of the litho type will control the quality of the flow path. Most mine drainage quality predictions, based exclusively on overburden analyses, assume a uniform wetting front and ubiquitous water flow within the spoil, when, in fact, water flow is preferentially oriented along the more permeable zones (determined by the rock's physical characteristics) which may be either acidic or alkaline. In so doing, the majority of the water flow comprising the seep (and its quality) comes in contact with a small portion of the total backfill or spoil material.

Extending this concept further to reclamation and in-situ acid abatement technology, to affect changes in chemical reactions, the chemistry of the water flow within the mine setting must be completely modified and controlled, an engineering challenge because, as discussed above, the runoff-infiltration ratios vary according to time of the year and nature of the precipitation. Accordingly, manipulation of the physical dimension is the only viable alternative. The number of studies providing for an understanding of this regime are remarkably few. At this stage of development we strive to chemically control a flow path by chemically altering the recharge point. However, within 1 meter of penetrating the surface of a spoil, the direction and movement of water is completely unknown, confusing the evaluation of the efficacy of treatment. Did the treatment adequately intercept the targeted zones, was the treatment of sufficient magnitude, has the treatment gotten there yet?

At what time will we see a call for innovative studies designed to stabilize reactive pyrites, to characterize the hydrology of acid producing sites leading toward water manipulation to control seep quality, to evaluate the interaction between revegetation, soil development and pores gas changes to ascertain at what time in the future the acidity will become self treating, novel ideas for the reconstruction of an abandoned mined land engineered to increase alkaline loads and reduce acid loads. At this level the unifying theme of the hydrologic cycle links together several elements of the mine drainage problem and begins to integrate results leading toward a central objective. Alternatively, do we still proceed to corroborate the works of Braley, Carpenter, Temple, Koehler, Starky,.......

STREAM SEALING TO REDUCE SURFACE WATER INFILTRATION INTO UNDERGROUND MINES[1]

Terry E. Ackman and J. Richard Jones2

Abstract.--As part of the Bureau of Mines environmental research, a novel approach to identify and seal surface infiltration zones was tested at a stream, near Frostburg, MD, that partially overlies abandoned coal mine workings. Ground electromagnetic conductivity surveys were performed within a stream channel to identify water-saturated zones at relatively shallow depths of 25 and 50 ft (7.5 and 15 m). Zones of increased conductivity were found to be positively associated with areas exhibiting significant loss of flow. Conversely, zones which exhibited declining conductivity values delineated areas where there were no significant flow losses. Using this information, an experimental grouting procedure was used to place an expandable polyurethane several feet (less than a meter) beneath the streambed over 70 ft (23 m) of the stream channel. Before grouting, the section exhibited a 25 pct loss (800 down to 600 gal/min); post-grouting gaging demonstrated a net gain. The conductivity surveys represent a significant cost savings in gaging work necessary for delineating stream loss zones. Also, the cost of grouting was over 50 pct less than the costs associated with conventional rechannelization and clay-lining and rip-rapping techniques.

INTRODUCTION

Underground mining operations frequently induce streamflow losses, which generally infiltrate into underground workings and oftentimes become a source of perpetual water pollution (Hobba 1981, Hollyday and McKenzie 1973, Williams et al. 1986). Streams are considered to be the largest contributor to the overall volume of underground acid mine drainage (AMD), but no quantitative work has ever been performed to test this assumption (U.S. Environmental Protection Agency 1979). In addition to ground water and surface water pollution, large water influxes into the mine can represent hazards to mine workers, hydrostatic heads can "blow out" the outcrop barrier pillars causing subsidence, and overflows can induce surface landslides.

Partial to total streamflow losses can occur, and multiple infiltration zones (both natural and induced) usually exist in a stream channel. Frequently, stream losses are not readily apparent at the surface. It is also difficult to pinpoint infiltration zones from underground mines (assuming accessibility) since waterflow paths may deviate considerable distances through bedrock fracture systems. Although the gob or large caved areas are accessible through the bleeder entries, only limited visual observations are usually possible.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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Surface rechanneling and stream channel liners, such as wooden canals and clay and rock rip-rapping, have been constructed to reduce stream water loss. By reducing the volume of water that enters underground mines from the surface, the volume of water discharged and treated (if contaminated) at the mine site should be considerably reduced. The cost however, of lining entire streams or sections of streams that overlie the underground workings is high. The costs for preventing infiltration can range between $40 and $80 per linear foot for relatively small streams (e.g., 5,000 to 10,000 gal/min (315 to 631 L/s) flows). Significant efforts to reduce stream seepage have been put forth, using the above mentioned techniques, in the anthracite regions of Pennsylvania (Ash and Whaite 1953). However, only limited success had been obtained by these techniques. The long-term effectiveness of such liners is questionable during times of drought or intermittent flow since vegetation, burrowing animals, and insects can affect the integrity of the artificial channel bottoms. The U.S. Bureau of Mines has, in cooperation with other Federal and State agencies as well as with private industry, instituted a research program to identify those sections along a stream channel that appear to be high subsurface infiltration zones. By predetermining these high loss zones, the total length of stream channel that must be lined can be considerably reduced. Therefore, the grouting costs for reducing infiltration are targeted to those particular stream sections which have been identified as zones of infiltration. This paper reports on the methodology used to identify zones of subsurface infiltration, and the experimental results of sealing Staub Run, located near Frostburg, MD, with a polyurethane grout.

ENVIRONMENTAL SETTING

Staub Run is located in northwestern Maryland approximately 5 mi (8 km) south of Frostburg, MD (fig. 1). The section of Staub Run under study is approximately 0.6 mi (0.9 km) in length. Staub Run is considered a natural gaining stream since the stream does flow perennially to the point at which it traverses the old abandoned mined-out coal seam, which also outcrops in the stream channel. Intermittent flow is observed during the summer, within the stream channel section which overlies the abandoned workings, and drains into Georges Creek. Staub Run and Georges Creek are part of the Potomac River Watershed. Annual rainfall is about 41 in (105 cm). Staub Run lies within the Appalachian Plateau Physiographic Province. The area is part of the Georges Creek Basin syncline, the northern extension of the Potomac Basin.

A number of Pennsylvanian-aged coal-bearing strata underlie the area. The coal units extend downward from the Barton Coal within the middle Conemaugh Formation to the top of the Mount Savage Coal which marks the base of the Allegheny Formation (Toenges 1949, O'Hara 1900). The generalized thickness of these coal-bearing strata is some 775 ft (235 m).

The Pittsburgh Coal seam crops out in the upper portion of Staub Run. The outcrop is arcuate along the stream channel, such that the outcrop extends upslope along both sides of the mountain valley after surface exposure within the stream channel. The middle to lower portion of this small mountain stream overlies an abandoned turn-of-the-century coal mine (Carlos Mine). The depth of overburden for the 3,000-ft-(914-m-) long test site

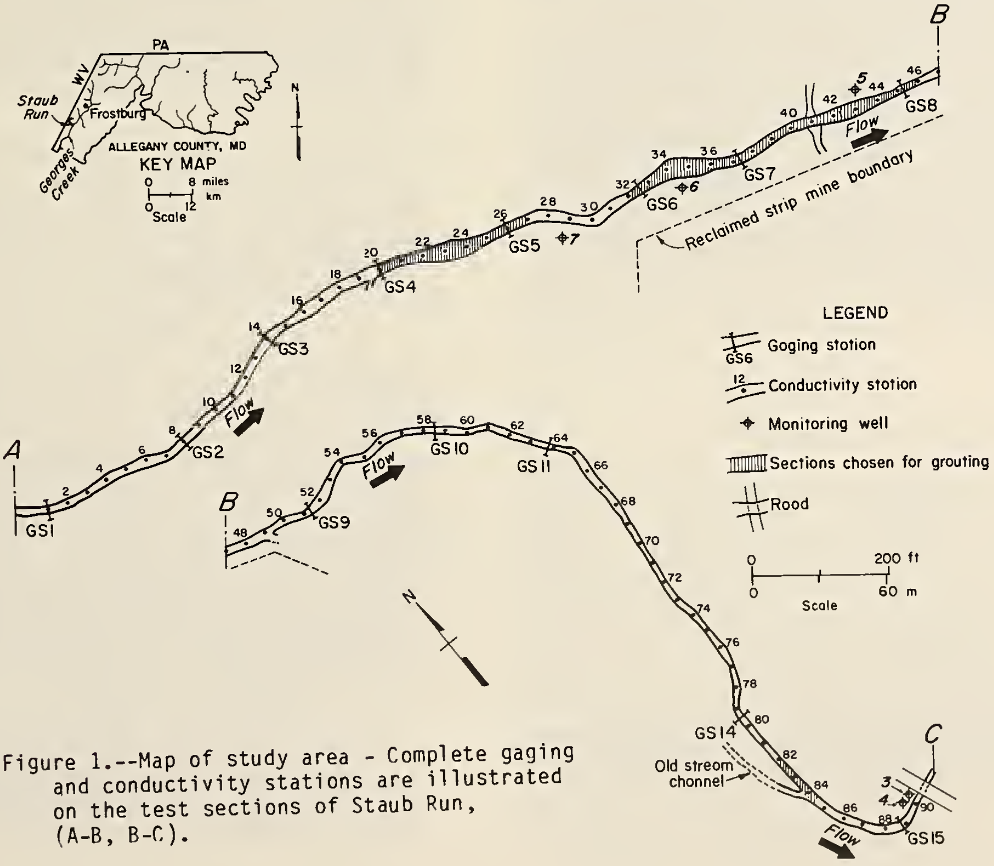

Figure 1.--Map of study area - Complete gaging and conductivity stations are illustrated on the test sections of Staub Run, (A-B, B-C).

ranges between 0 and 63 ft (19 m). Stripping activity (pillar recovery work) has taken place on both sides of Staub Run. In one portion of Staub Run, stripping operations have mined through the stream, thus necessitating re-routing of the flow which re-enters the natural stream channel approximately 1,000 ft (305 m) down gradient (fig. 1). The channel bottom can best be described as alluvial material; the sediments are sands, clays, pebbles, and various cobble-sized boulders. The thickness of this alluvial material, based on former and current drilling records, averages some 12 ft (4 m) at the study site.

METHODOLOGY

Streamflow Gaging

Fifteen stream gaging stations spaced at approximately 200-ft (60-m) intervals were established along Staub Run (fig. 1). Stream gaging began on October 23, 1986, and continued through September 17, 1987. Discharge was measured using a portable flow meter equipped with an electromagnetic sensor, following standard procedures established by the U.S. Geological Survey for determining the velocity/area of the stream. Measurements were taken at about 5-day intervals.

Gaging efforts focused on establishing a flow profile for the study area. The initial profiling efforts included routine flow monitoring of gaging stations 1, 5, 8, 14, and 15 (fig. 1). Stations 1 and 5 served as the control stations (outside the influences of mining operations) while station 15 represented the last gaging station in the study area. It became apparent from gaging data, collected during the first full dry season, that significant loss zones existed in upper portions of the study site. This gaging data targeted the zone(s) for future grouting. Thus, gaging efforts were expanded, beginning in March 1987, to focus upon the upper study site by routinely monitoring gaging stations 1, 5, 6, 7, and 8 (fig. 1), as well as stations 14 and 15 (fig. 2). A series of one-tailed t-tests were computed to test if the downstream station discharge was significantly greater ($p \leq 0.05$) than the corresponding upstream station discharge.

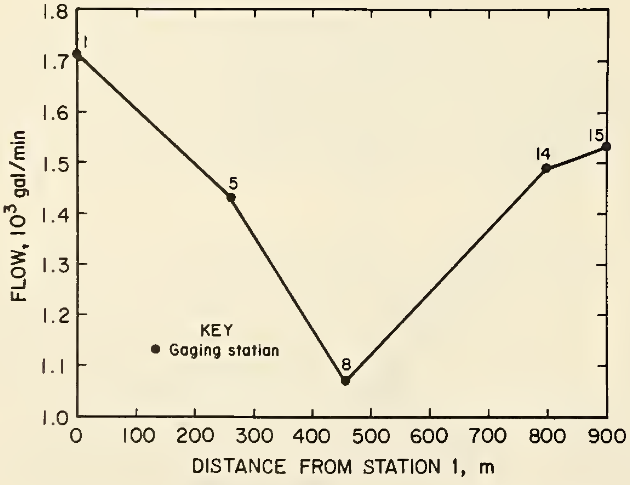

Figure 2.--Mean annual discharge at Staub Run.

Electromagnetic Ground Conductivity Surveys

Electromagnetic ground conductivity surveys were used in a novel attempt to identify stream loss zones by delineating the presence of water-saturated zones directly beneath the stream channel. The equipment consisted of a transmitter, transmitter coil (wire loop), receiver, receiver coil, and connecting cable. A two-person crew is required for using this entirely portable equipment. One person carries the transmitter and transmitter coil and the other person carries the receiver and receiver coil. Readings were taken at a fixed distance of 33 ft (10 m) between transmitter and receiver coils; however, fixed distances of 66 ft (20 m) and 132 ft (40 m) are also available for greater depths of penetration with this equipment.

The surface transmitter induces a current in the subsurface material with this electromagnetic induction technique. An alternating magnetic field is produced from the alternating current generated from the transmitter coil. The magnetic field induces current flow through the substrate as it penetrates the ground surface. The receiver coil senses a secondary magnetic field which is generated by the induced currents. The secondary magnetic field sensed at the coil is a function of: the strength of the primary field; current frequency, distance between transmitting and receiving coils, and ground conductivity. The ground conductivity is the only unknown variable since the primary field, frequency, and coil separation can be controlled. The receiver, which senses the secondary magnetic field, internally converts the signal to terrain conductivity and digitally displays signal in millimhos/meter (mmhos/m). The reader is referred to standard geophysical texts for detailed derivations (McNeill 1980, Grant and West 1965, Keller and Frischknecht 1966, Ladwig 1982) since the mathematical theory behind the induction technique is beyond the scope of this paper.

Theoretically, the magnitude of the ground conductivity should increase when saturated conditions exist. Consequently, the water loss zones should be zones of high conductivity. Thus, the conductivity data and gaging data should have an inverse relationship.

Two series of conductivity measurements were taken within the stream channel between the 15 gaging stations at 33-ft (10-m) spacings. One series of measurements was taken during the wet season and the other during the dry season (figs. 3 and 4). A Geonics EM-34 electromagnetic ground conductivity meter was used to obtain measurements at about 25- and 50-ft (7.5- and 15-m) depths. The observation depth is changed by changing the orientation of the instrument. Several portions of Staub Run, between conductivity stations 2 and 5 and between stations 64 and 69, may have registered erroneous readings with the conductivity instrument due to metallic interference (steel pipes, old appliances, and metal debris).

A statistical comparison between the conductivity and gaging data was performed. The conductivity data from the wet and dry seasons were combined to generate an annual mean conductivity (fig. 5). This was done by taking the difference

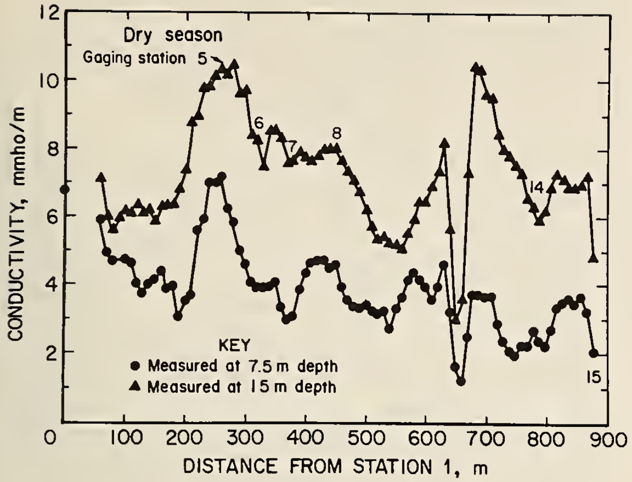

Figure 3.--Conductivity survey (dry season) at Staub Run.

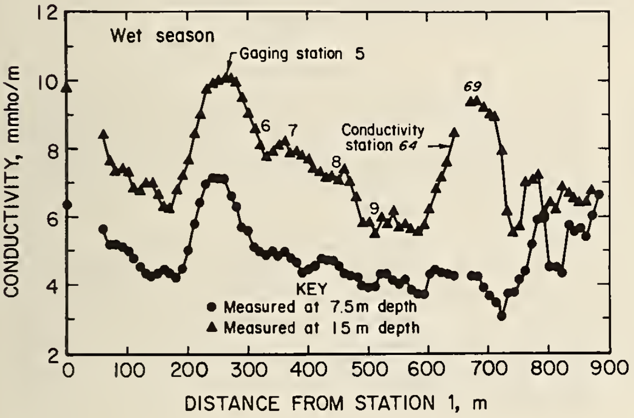

Figure 4.--Conductivity survey (wet season) at Staub Run.

between the two observation depths as a means of normalizing the data. The differences between the vertical and horizontal readings for each station of both series were then added together and divided by 2 to obtain a mean conductivity.

$$\text{Mean Conductivity} = (\overset{\text{WET}}{(V - H)} + \overset{\text{DRY}}{(V - H)})/2$$

Since the number of stations where conductivity measurements were recorded exceeded those where stream gaging occurred (figs. 1 and 2), comparison between the two data sets was accomplished by using polynomials to predict the statistically best-fit equation for the respective data. In this way the conductivity measurements and the gaging records were each treated as separate mathematical curves. Once a polynomial curve is fit to the respective data, a predicted trend pattern emerges between the two measures whose station to station relationships can be further tested. The mathematics and examples of polynomial curve fitting applications in the earth sciences are numerous (Doornkamp and King 1971, Jones and Cameron 1977, and Fisher et al (in press)).

Corresponding measurements were most complete between gaging stations 1 through 8 and conductivity stations 1 through 45, so these data were used to generate the respective polynomial equations. Furthermore, the mean station gaging discharge (October 23, 1986 to September 17, 1987) and the mean station conductivity measurement (wet season, dry season) are considered representative of the seasonal trends so the respective averages are used as the dependent variables with the conductivity station locations serving as the independent variables. After determination of the best-fit equation for the respective data, predictive values are generated for the station measurements and then compared with Spearman's Rank Order correlation analysis.

Grouting Procedure

Experimental grouting was conducted between gaging stations 14 and 15 (fig. 1). Grout rods 3 ft (1 m) in length were used for injection of the polyurethane material into the alluvial stream sediments. The rods were 3/4-in (1.9-cm) diameter steel pipes with hardened steel points with 1/8-in (0.3-cm) holes drilled through the sidewalls near the lower portion of the rod. The top of the threaded rods incorporated a hardened steel cap which would withstand blows from a sledge hammer and could also be used for mechanical injection of the polyurethane grout. The rods were manually driven into the stream sediments with a sledge hammer to a uniform depth of 2 ft (0.66 m) beneath the stream channel and placed at 10-ft (3-m) centers.

A measure of 5 gal (19 L) or 44.5 lbs (20.2 kg) of a two-component polyurethane grout, 2.5 gal (9.5 L) of each component, was injected into each grout rod. Injection pressures ranged from 400 to 1,200 lb/in^2 (28 to 84 kg/cm^2) with the in situ conditions of alluvial material dictating the pressure. The pump which was used was capable of 2,000 lb/in^2 psi (141 kg/cm^2). Grout was injected at a maximum pressure obtainable until a surface leak developed. After the leak occurred, the injection pressure was reduced to 50 lb/in^2 (3 kg/cm^2) until the leak sealed itself. The pressure was then increased slowly until another leak occurred or the 5 gal (19 L) of material was depleted.

RESULTS

Gaging and Conductivity

In most natural streams there should be a downstream increase in the volume of discharge. To test if the between- station volumes along Staub Run followed this natural pattern, a series of one-tailed t-tests was computed for the contiguous gaging stations 1 to 5, 5 to 6, 6 to 7, 7 to 8, and 5 to 8 (table 1). The one-tailed t-test not only determines if a significant difference ($p \leq 0.05$) exists in discharge measurements between the respective gaging stations, but is directional in that one can test if the discharge at one gaging station is significantly greater than that of another gaging station.

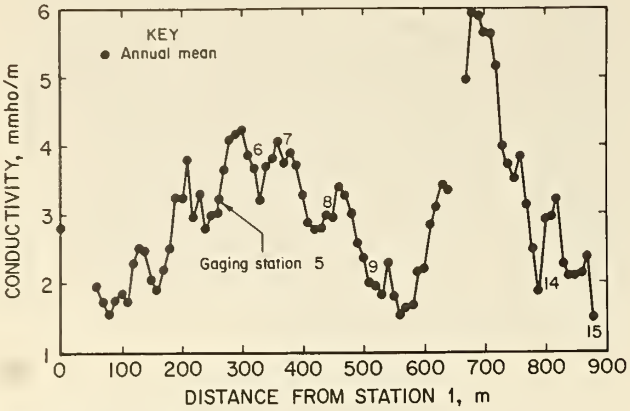

Figure 5.--Mean annual conductivity Staub Run.

Since flow rates should increase in a downstream direction, the test was formulated such that the contiguous downstream station discharge should be significantly greater than the corresponding upstream station discharge. If it can be demonstrated that the reverse is statistically significant, i.e., the upstream station has larger discharges, then it is assumed that the stream segment between the two gaging stations is experiencing a flow loss and thus represents a zone of significant subsurface infiltration. For the t-tests between the two contiguous stations, discharge data are only used when measurements were recorded on the same day at the two stations (table 1).

The results of the t-tests are interpreted to show that significant downstream losses occur between stations 1 and 5, and stations 6 and 7. Significantly greater upstream discharges were not identified between stations 5 and 6 and stations 7 and 8 (table 1). Following the original hypothesis, the stream segments located between stations 1 and 5 and stations 6 and 7 represent zones of statistically significant subsurface infiltration. Although the downstream flow rates are apparently less than the corresponding upstream flow rates between stations 5 and 6 and stations 7 and 8 (table 1), the differences are not statistically significant ($p \leq 0.05$). To further test an overall flow loss pattern, a one-tailed t-test was also computed between stations 5 and 8, again using only those gaging measurements when recorded on the same day at the respective stations (table 1). The t-test results illustrate a significantly ($p \leq 0.05$) higher flow at station 5 as compared to the flow at station 8 (fig. 2). This appears to confirm that infiltration zones are occurring downstream between station 5 and station 8 along this portion of Staub Run.

As noted in table 1, there is a significant discharge loss occurring between gaging stations 1 and 5 (fig. 2). The local bedrock and structural geology indicate that coal could not have been extracted from beneath this area. Examination of stereo paired aerial photographs (1:1000, 1983 series) appears to show the presence of a linear, crossing the stream in the vicinity of gaging station 5. The area of the apparent linear has, however, been significantly altered by man through surface mining, timbering, and the construction of residential and other types of structures so it is difficult to confirm its existence. Field reconnaissance of the area was also unable to follow a continuous linear trace.

The preliminary analysis of the gaging data and conductivity surveys does show a significant loss zone in this area so additional analysis of the aerial photographs for confirmation of the linear is presently being made.

The discharge measurements are best defined by a second-degree equation. The multiple coefficient of correlation (R^2) for the second-degree equation is 0.94. The predicted discharge values by station are presented in table 2 with the predicted curve trend illustrated in figure 6.

The mean conductivity measures are best defined by a sixth-degree equation. The multiple coefficient of correlation (R^2) for the sixth-degree equation is 0.71. The predicted conductivity measurements by station are presented in table 2 with the predicted curve trend illustrated in figure 6.

Comparison of the predicted curve trends between the discharge and conductivity measurements appear to show a negative relationship (fig. 6), i.e., a station increase in conductivity appears to correspond to a decrease in station discharge. To test if this apparent trend is significant, the non-parametric Spearman's Rank Order Correlation was computed (Doornkamp and King 1971).

Table 1.--Paired t-tests for gaging data.

Statistical pairs (gaging stations)	Average flow, gal/m	Maximum flow, gal/m	Minimum flow, gal/m	Sum of flows, gal/m	Number of gaging events	Statistically significant
1	1,060	4,353	6	45,589	43	Yes
5	923	3,629	5	39,687		
5	424	1,695	5	5,939	14	No
6	409	1,384	8	5,720		
6	394	327	35	5,905	15	Yes
7	327	1,114	21	4,905		
7	471	1,114	35	4,713	10	No
8	462	1,249	1	4,616		
5	946	3,629	64	34,986	37	Yes
8	696	2,506	1	25,763		

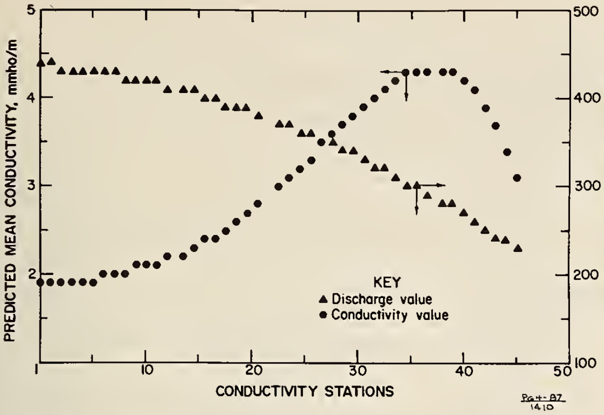

Figure 6.--Predicted curve trends between the discharge and conductivity measurements. The predicted second-degree equation for the discharge is given by: $y = 438.16 - 0.887x - 0.084x^2$, where y = predicted mean discharge and x = station location. The predicted sixth-degree equation for the conductivity is given by: $y = 1.85 + 0.013x + 11.97x^2 + 0.00008x^3 - 17.7x^4 - 18.00x^5 - 0.0000000009x^6$, where y = predicted mean conductivity measurement and x = station location.

The Spearman's Rank Order Correlation coefficient is -0.92 suggesting a strongly negative relationship between the station discharge and conductivity measurements. Thus, the predicted curve trends of the two measurements illustrated in figure 6 do show a negative relationship, such that high conductivity readings generally correspond to lower discharge measurements. In terms of identifying subsurface infiltration zones, the stations exhibiting lower discharges and higher conductivity measurements are areas where streamflows are infiltrating into the underground workings. Alternatively, the stations exhibiting higher discharges and lower conductivity measurements are areas where stream water does not appear to be infiltrating or there is less infiltration into the mine.

Grouting

In order to establish a methodology for surface grout injection, a section of stream channel between conductivity stations 82 and 84 was selected as the test area (fig. 1). Prior to the grout injection procedure previously described discharge measurements were taken at conductivity stations 82 and 84 on May 20 and May 28, 1987 (table 3). The polyurethane grout was injected into the stream at 10-ft (3.3-m) centers between conductivity stations 82 and 84, i.e., seven grout rods were used along the 70-ft (23-m) section of stream following gaging on May 28, 1987. Post-grouting gaging was conducted on May 29, June 4, and June 5, 1987 (table 3). As illustrated in table 3, the discharge rates between conductivity stations 82 and 84 showed a net gain in flow after grouting was completed.

Unfortunately, stream discharge decreased to low flow conditions within the grout test area around mid-June 1987 (approach of the dry season) and eventually the stream flow terminated. The overall gain in discharge between these two stream points for the time of gaging does, however, suggest that the grout injection procedure does prevent subsurface infiltration.

Based on this limited sealing operation, costs are estimated to range between $25 and $30 per linear foot of the 10-ft (3.3-m) wide stream channel. Other streams in the watershed of approximately the same size and geological conditions have been rechannelized with heavy equipment and sealed with clay-lining and rock rip-rapping. The costs of these sealing operations were over $70 per linear foot. In addition to significantly disturbing natural conditions, the effectiveness of the latter technique is questionable based on visual observations of the streams during various flow conditions. Future evaluation of the conventional stream sealing techniques are scheduled.

CONCLUSIONS

This novel approach to identifying infiltration zones has demonstrated that areas of high conductivity trends were associated with significant stream losses, and that areas of declining conductivity trends demonstrated no significant losses in stream flows. This technique demonstrates a potential for accurately locating stream loss zones without flow monitoring for a full hydrological year. The two conductivity surveys (wet and dry season) over the 3,000-ft (910-m) stream segment took only a day each to complete. Thus, by performing conductivity surveys coupled with confirmation gaging, areas of stream infiltration were located with minimal time and effort. In addition, this pinpointing of loss zones was indiscriminate of natural or manmade causes. This implies that the potential for identifying natural fracture zones (linears) exists, and this technique may be a predictive tool for possible roof control problems in active underground workings.

The stream sealing technique which has been developed was demonstrated to be quick and easy, causing minimal disturbance to the natural conditions. This novel approach shows good potential for reducing surface and ground water infiltration into underground workings (both active and abandoned). Limited data have been encouraging in terms of effectiveness. In addition, the potential for 50 pct cost savings exists when compared to conventional clay-lining and rock rip-rapping techniques. Consequently, this technique offers an economical means of reducing pollution in abandoned mines, as well as reducing water-handling and treatment costs in active mines.

Based on data collected thus far, full-scale grouting targets have been identified in the upper project site between conductivity stations 20 to 27 and 32 to 45 (fig.1). This grouting work is scheduled to be completed in the near future and will affect 800 ft (242 m) of stream channel while only actually sealing 600 ft (182 m). Although this project appears promising for alluvial type stream channels, more work needs to be performed with bedrock stream channels. In addition, the bedrock situation is anticipated to be slightly more expensive due to obvious drilling operations which would be required.

Table 2. -- Predicted mean conductivity and mean discharge measurements.

Conductivity station	Gaging station	Predicted conductivity, mmho/m	Predicted discharge, gal/m	Mean Measured discharge gal/m
1	1	1.86	437.19	433
2		1.88	436.05	
3		1.89	434.74	
4		1.91	433.27	
5		1.92	431.63	
6		1.95	429.81	
7		1.97	427.83	
8		1.99	425.69	
9		2.02	423.37	
10		2.06	420.89	
11		2.10	418.24	
12		2.14	415.42	
13		2.19	412.43	
14		2.25	409.28	
15		2.31	405.96	
16		2.37	402.46	
17		2.44	398.81	
18		2.52	394.98	
19		2.61	390.98	
20		2.70	386.82	
21		2.80	382.49	
22		2.90	377.99	
23		3.00	373.32	
24		3.12	368.49	
25		3.23	363.49	
26	5	3.35	358.31	394
27		3.47	352.97	
28		3.58	347.47	
29		3.70	341.79	
30		3.82	335.95	
31		3.93	329.94	
32	6	4.03	323.76	305
33		4.12	317.41	
34		4.20	310.90	
35		4.26	304.21	
36		4.31	297.36	
37		4.33	290.35	
38	7	4.33	283.16	250
39		4.29	275.80	
40		4.21	268.28	
41		4.10	260.59	
42		3.93	252.73	
43		3.71	244.70	
44		3.43	236.51	
45	8	3.08	228.14	249

Table 3. -- Pregrouting and post-grouting discharge change.

	Conductivity station 82 discharge, gal/m	Conductivity station 84 discharge, gal/m	Change, gal/m
May 20, 1987	1,228	1,194	-34
May 28, 1987	845	634	-211
*May 29, 1987	618	693	+75
*June 4, 1987	237	332	+95
*June 5, 1987	262	280	+18

*Post-grouting discharges.

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UNSATURATED FLUID FLOW IN MINE SPOIL: INVESTIGATIVE METHODS LEADING TO A QUANTITATIVE CHARACTERIZATION

David M. Diodato *and* Richard R. Parizek[1]

A tracer study using non-radioactive neutron activatable bromide-79 was employed as an investigative technique to determine *in situ* unsaturated hydraulic conductivities at a reclaimed and revegetated strip mine in Clarion, PA. This investigation is a part of an ongoing acid mine drainage abatement study using surficial lime plant flue dust and limestone quarry waste. Water samples were collected through time from 55 pressure-suction lysimeters installed at various depths at the field area. 23 were selected for study and neutron activation analysis was used to determine Br concentration. Interpretation of the concentration peaks as average arrival times of infiltrating rainwater yielded unsaturated hydraulic conductivities ranging from 0.0279 to 0.5313 ft/day with one value of 1.1625 ft/day. This high value is interpreted as an example of infiltrating water piping through the highly heterogeneous disturbed spoil pile. Excluding the high and low values, the mean and the median unsaturated hydraulic conductivities were found to be 0.1876 ft/day and 0.1582 ft/day, respectively. These values are in the range of 0.14 to 18.76 percent of saturated hydraulic conductivity of the various geologic materials at the site. Further refinement of the data may be yielded by geostatistical investigations, as the semivariogram of the concentration values at a sampling point through time may suggest alternative concentration peak dates. A second investigative technique, the use of neutron depth-density and depth-moisture probes, will be of use in the determination of soil bulk density and soil moisture content values. An increased understanding of the behavior of alkaline waters and the hydraulic conductivity in the unsaturated zone will help investigators to evaluate past abatement strategies and to plan future ones.

INTRODUCTION

The unsaturated hydraulic conductivities of a reclaimed and revegetated acid-producing strip mine are being investigated and quantified by means of a tracer experiment. This research is in conjunction with a large-scale acid mine drainage abatement experiment the C&K Coal Old Forty Strip Mine site, Clarion, PA. The latter seeks to quantify the effects of two surficial treatments, each using different application amounts of lime plant flue dust and limestone quarry waste, in abating the acid production of the strip mine. On a macroscopic level, the alkaline waters resulting from precipitation on the applications in the two treatment plots may have been expected to percolate down through the spoil pile as a relatively uniform front. However, inspection of chemical analyses of soil water samples from the site suggested that the downward flow of these waters was not uniform. A desire for an increased understanding of the nature of unsaturated fluid flow at the site was the motivation for the bromide tracer experiment.

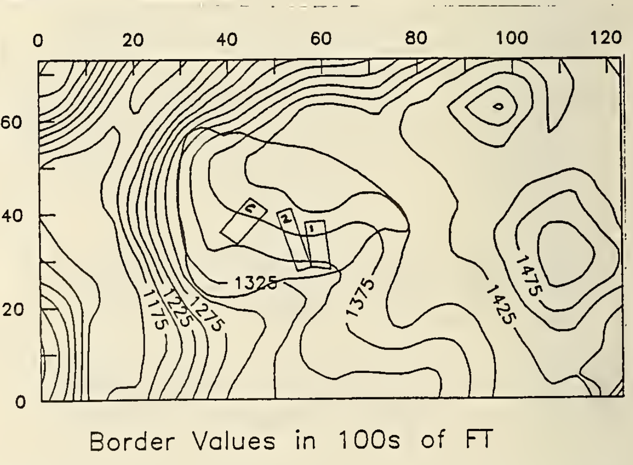

Figure 1. Site map showing limits of mining, treatment plots 1 and 2. and the control plot, C.

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At the site there are 17 drill holes that contain nests of pressure-suction lysimeters. These are buried at approximately 7-ft depth intervals. Figure one is a map of the site showing the treatment plots and lysimeter nest locations. The drill holes were backfilled preferentially using drill cuttings and other spoil materials readily available at the site. In some cases, it was necessary to use additional, exotic sand and gravel. But, in general, the use of materials found at the site helped to ensure that drill holes remained representative, both chemically and hydraulically, of the adjacent spoil pile.

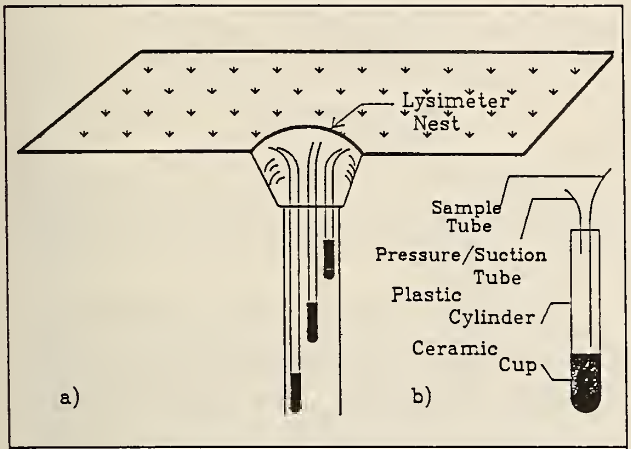

Figure 2. a) Schematic pressure-suction lysimeter nest installation. b) Cut-away view of a pressure-suction lysimeter.

Figure two is a schematic of a lysimeter nest installation. Soil water samples have been collected from these devices on a bi-weekly to monthly basis since 1984. What has been observed in some of these nests is an increased alkalinity at shallow depths, more acidic conditions at intermediate depths, and increased alkalinity at greater depths. This anomalous result immediately suggests three hypotheses. One hypothesis is that these lower alkalinity and pH samples could be produced by isolated hot spots in the spoil pile. If this is the case, then optimal remedial efforts should center on the identification and treatment of these hot spots, which may be responsible for the bulk of acid production. Alternatively, these low alkalinity zones could reflect decreased circulation of alkaline charged waters resulting from the treatment. This might result if these zones were more shaly, the disaggregated shale having a lower hydraulic conductivity than adjacent disaggregated blocky sandstone. Finally, this finding could be a result of a combination of the two previously mentioned factors, with the shaly zones containing the bulk of the pyritic material. The second hypothesis may be evaluated by determining the *in situ* unsaturated hydraulic conductivity of many zones in the spoil pile. In addition, knowledge of representative unsaturated hydraulic conductivity values will be of use to workers in this field.

THEORETICAL BACKGROUND

A tracer experiment is underway which aims to map hydraulic conductivities through the spoil pile. The chosen tracer was the non-radioactive, neutron activatable bromide-79. The advantages of bromide-79 as a tracer are outlined in the literature Schmotzer *et al.* (1973) and Jester *et al.* (1977). Briefly, they are as follows. Background bromide typically exists in natural aqueous systems at very low levels (40 to 300 ppb) in geologic association with evaporitic brine and marine shale sequences. Neutron activation analyses of background samples from the site showed no detectable bromide. It is not toxic to humans below 0.5 to 1.0 mg/mL of blood. Bromide is conservative in that it does not readily adsorb, absorb, or precipitate to a significant degree on natural surfaces. Bromide is unaffected by the actions of microbial biota. Further, the sensitivity of detectors allows resolution of background bromide to as low as 20 ppb. In addition to this, analysis and initial purchase cost of bromide are relatively inexpensive (Schmotzer *et al.* 1973). 25 pounds of potassium bromide were purchased for this experiment for less than two hundred dollars. Ammonia bromide is even less expensive, but potassium bromide was chosen to eliminate any slight nitrification of ground waters which may otherwise have occurred.

The quantification of unsaturated hydraulic conductivity in this study is accomplished by direct measurement of *in situ* bromide contents of infiltrating waters through time, the peaks of which are inferred to represent average transport times. This inference is not without precedent (Schmotzer *et al.* 1973, Jester *et al.* 1977, Brasino and Hoopes 1985, Raupach *et al.* 1983).

Saturated Hydraulic Conductivity

Hydraulic conductivity is a parameter of the D'Arcy fluid flow relation which describes the capacity of a given medium to transmit a given fluid. It is expressed in the units of a velocity, length per time. Hydraulic conductivity is a function of the characteristics of both the medium and the fluid moving through it. This is well illustrated by the relation

$$K = (\kappa \rho g)/\mu \tag{1}$$

where

K = Hydraulic Conductivity
κ = Intrinsic Permeability
ρ = Fluid Density
g = Acceleration Due to Gravity
μ = Fluid Dynamic Viscosity

(Freeze and Cherry 1979)

Here the intrinsic permeability, κ, is a function of the medium alone, and includes factors describing mean grain diameter, the packing arrangement of grains, and the sphericity and roundness of grains, among other factors. It is a term best suited to the idealized D'Arcian elemental volume concept, and less well suited to more complex fluid flow such as that which exists in fracture flow controlled terrains. The terms which describe fluid properties are density, ρ, and dynamic viscosity, μ. These properties are well known and tabulated for a number of fluids at standard temperature and pressure, and for water at standard pressure over a wide range of temperatures. For water flow in a near-surface, non-hydrothermal, non-brine environment, these properties may be safely assumed to be constant. Similarly, the earth's gravitational force, which is acting on the fluid, decreases exponentially with distance away from the core, but may be considered constant within a small range of elevations.

Unsaturated Hydraulic Conductivity

For any given medium and fluid, saturated hydraulic conductivity represents the limiting case in that it is the maximum measure of this fluid transmitting capacity. As a medium becomes increasingly unsaturated with respect to a fluid, the volume of the medium transmitting the fluid decreases. Because there is a loss of fluid transmitting volume measured in L^3, expressed in a term of L/T, the decrease in hydraulic conductivity with increasing unsaturation is often dramatic and may span several orders of magnitude or more.

The degree of unsaturation can be expressed by a number of parameters, two of which are volumetric water content, θ, and matric potential, Ψ. Volumetric water content is the volume of water in a unit volume of medium, commonly expressed as a percentage. Thus if a medium has a porosity of 20 percent, and a volumetric water content of 20 percent, it is fully saturated. Increasing air content reflects increasing unsaturation. It should be noted that porosity does not imply permeability, because the void spaces are not necessarily interconnected.

Alternatively, matric potential is a measure of the tension at which water is held within the medium. In the literature, the symbol Ψ is commonly used to express the pressure head portion of the total hydraulic head relation, and thus includes both positive and negative pressure regimes. Here, we use Ψ to indicate only the nonpositive pressures which exist in the unsaturated zone. In adherence with established conventions, matric potential pressures are expressed as equivalent height of a column of water. This is a function of the mean grain size of the medium, among a number of other factors, and can be expressed by a capillarity relation.

$$\Psi = (2\ \sigma \cos\theta)/(r\ \rho\ g) \qquad (2)$$

where

Ψ = Height of Capillary Rise
σ = The Surface Tension of the Water-Rock Interface
θ = The Angle of Contact of the Capillary Force
r = The Radius of the Pore
ρ = Fluid Density
g = Acceleration Due to Gravity (after Miller 1982)

Consistent with potential theory, fluid will flow from higher to lower matric potential pressures. Thus one way to view matric potential is as the nonpositive part of the continuum between negative and positive fluid pressures, with zero matric potential at the water table. Commonly, above the water table there exists a tension-saturated zone where water is stored in the medium under capillary force. Both matric potential and volumetric water content can be measured with field instrumentation and are of direct bearing on unsaturated hydraulic conductivity. Thus, unsaturated hydraulic conductivity is commonly expressed as a function of matric potential, K(& Ψ&), or as a function of volumetric water content, K(& θ). By either measure, saturated hydraulic conductivity is the upward limiting case.

The phenomenon of unsaturation has many important and complicating consequences. Among these, one of theoretical significance is the behavior of a slug of water associated with a single infiltration event. This slug will have a leading wetting front and a trailing drying front as it percolates downward through the unsaturated zone. A graph of either volumetric moisture content or matric potential versus unsaturated hydraulic conductivity has two hysteretic curves, one describing each front. This is because the wetting front has a greater hydraulic conductivity than the drying front. Because the tracer experiment is not strictly infiltration event-oriented, an investigation into this transient phenomenon is beyond the scope of this study.

EXPERIMENTAL METHODS

Two sets of background samples were collected from the 55 pressure-suction lysimeters installed at the site, the first on November 5, 1985 and the second on April 5, 1986. Subsequently, on April 4, 1986, a 4,080 mg/L aqueous bromide solution was applied around each of the lysimeter nests, except for TR2LY5, which has only one functioning sampling device. The application pattern is illustrated schematically in figure 3. The application was in a radial hexaseptate pattern designed to emulate a diffuse source. The bromide application emulated a diffuse source in an effort to mimic the behavior of both the rainwater and the limestone quarry waste and flue dust abatement application, all of which are diffuse sources. Each radius was 25 ft in length and received 5 gal of solution. Care was taken to avoid application immediately on the lysimeter nest, so as to avoid any possibility of downhole piping or channeling through backfill sediments. Soil and meteorological conditions at the time of the application were ideal. The land surface was dry and rapid infiltration occurred with no runoff observed. Coincident with the completion of the application, a very gentle rain began to fall. This drizzle increased in intensity at a slow and steady rate over the next 6 to 12 hours, ensuring maximum infiltration of the tracer.

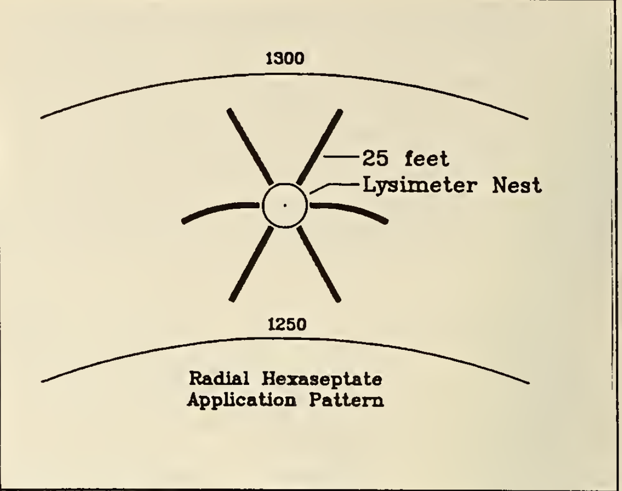

Figure 3. Schematic of tracer application pattern with contour lines.

Water samples were collected from the pressure-vacuum lysimeters installed in the 17 lysimeter nests at the site, from surface waters which flow through and off the site, and from ground water wells. The collection schedule varied according to precipitation and evapotranspiration, but averaged about three times a month during the initial four month period beginning April 14, 1986. For the next eight months sampling was conducted on a monthly basis. After April 14, 1987, one full year of bromide sampling had been completed, and the sampling schedule was reduced to a bimonthly one. The last sampling was in August 1987. A careful sampling procedure ensured that the integrity of the samples is maintained during collection. Because of the stability of the bromide anion, samples are safely stored at room temperature for several months.

The sampling procedure involves several anti-contamination safeguards. Sample bottles are kept sealed prior to and following sampling. While the lysimeter sampling tubes are held earthward, they are rinsed with distilled water and dried with paper towels. This cleaning is designed to eliminate the presence of contaminants which may have been derived from surficial sources. Initially, as the sample is being drawn, a small volume is discharged to the ground in order to further flush the sample tube. During sampling, the lids of the bottles are kept off the ground, as the ground potentially contains very high levels of Br^-. The sample is collected in the bottle, taking care to prevent the outside of the sample tube from coming in contact with the inside of the bottle, and the lid of the bottle is reattatched.

Neutron activation analysis is a straightforward procedure. Five mL portions of the samples are placed in 2 dr poly vials and irradiated with gamma radiation. Neutron activation produces a number of short-lived isotopes of bromide-79, including bromide-80 and bromide-82. A 50 cm^3 ge(li) detector counts the disintegrations, and feeds the data to an ND-680 pulse height analyzer. Because each isotope has a unique spectrum of escape energies, isotopes may be readily identified. By comparing the magnitude of peaks of a particular escape energy with the magnitude of peaks of the same escape energy produced by a standard of known concentration, concentrations can easily be calculated.

The method of calculation for bromide concentration in neutron activated water is simplified by holding several of the variables constant. For any given run, all samples, including standards, are activated at a constant flux energy level for the same amount of time, and counted with the detector mounted at a constant distance for the same amount of time. A correction must be made for decay times for all of the samples, including the standards. Most sample group activations were performed at 900 kW for 1 minute, although some were at 1,000 kW for 1 minute. In every case, counts lasted 45 minutes. The governing relation for radioactive decay is

$$N = N_0 \exp[-\lambda t/T_{1/2}] \qquad (4)$$

where

N = The observed sample activity after decay time, t.
N_0 = The initial sample activity.
λ = A decay constant, 0.693.
t = Decay time, time elapsed between sample activation and counting.
$T_{1/2}$ = The half-life of the isotope of interest.

Having completed a series of activations and counts, the initial activity of the standard must be calculated. Rearranging (4),

$$N_0 = N \exp[\lambda t/T_{1/2}] \qquad (5)$$

Here, N_0 is the number of counts that the 50.0 parts per million standard would have produced at $t = 0$. Next, the initial activity of the sample is calculated, using the previous relation. Finally, the bromide concentration of the sample is calculated using the relation

$$[\text{Br } \textit{sample}] = N_0 \textit{ sample } (50.0 \text{ ppm} / N_0 \textit{ std}) \qquad (6)$$

When a preliminary run revealed some interference from manganese (an isotope of which has an escape energy close to that of bromide-80) in the water, it was decided to count the longer lived isotope bromide-82 after waiting a day for the manganese-56 to decay. Because of this, it was necessary to make a correction to allow for the decay time prior to counting for all of the samples, including the standards.

Six lysimeter nests were identified as representive of the range hydrologic and lithologic conditions found at the site. These were selected for intensive study. Their identification numbers, TR1LY1, TR1LY3, TR2LY1, TR2LY4, CLY5, and CLY6, are an artifact of the acid mine drainage abatement experiment, reflecting the existence of two treatment plots and one control plot. These nests contained a total of 23 functioning pressure-suction lysimeters buried at successive depths. A total of 257 neutron activation analyses have been successfully completed. This includes 17 ground water samples, 4 background samples, 2 application samples and 234 soil water samples. This represents an average of over ten analyses per lysimeter. In addition, some sample activations were duplicated to ensure the validity of the results.

INTERPRETATION OF RESULTS

The use of concentration peaks to infer unsaturated hydraulic conductivities hinges on several assumptions. These can be divided into three categories pertaining to the behavior of the tracer, the integrity of the sampling program, and the behavior of the fluid flow in the reclaimed and revegetated strip mine. First, it is necessary to assume that bromide is a truly conservative tracer. With this in hand, we can assume that concentration peaks at a particular sampling point are proportional to average arrival times of tracer-bearing waters. Second, sampling protocol must be rigorous enough to prevent contamination of samples, which would lead to erroneous results. Also, the sampling schedule must be sufficiently dense to successfully define concentration peaks. In this case, the sampling schedule was limited not only by labor considerations, but also by the sampling devices themselves. Pressure-suction lysimeters collect water from the unsaturated zone at a decreasing rate with increasing unsaturation, as was the case in the early summer months of the study. However, the many well-defined peaks produced by this study suggest that the sampling schedule was sufficiently dense. Finally, for purposes of calculation of unsaturated hydraulic conductivity, it is necessary to assume that fluid flows in the shortest path from the land surface to the buried lysimeter. This assumption eliminates the evaluation of the nearly infinite variety of flow paths which infiltrating waters may have followed. Further, it is assumed that fluid flow occurs in a continuous and not discrete or pulsed manner. With a time scale on the order of days, this assumption may not be unreasonable. These two assumptions concerning the behavior of fluid flow will tend to skew the values obtained for unsaturated hydraulic conductivity downwards.

With these assumptions in mind, the unsaturated hydraulic conductivites which exist around the pressure-suction lysimeter sampling points may be calculated by simply observing the time of the concentration peak at a particular lysimeter and dividing the depth at which the lysimeter is buried by this time. The unsaturated hydraulic conductivities presented in ascending order in table one are calculated based on the sampling date which yielded the highest concentration of bromide.

Table 1. Computed unsaturated hydraulic conductivities.

Lysimeter Nest	Lysimeter Number	Lysimeter Depth (ft)	Unsaturated Hydraulic Conductivity (ft/day)
CLY5	74	14.0	0.0279
CLY5	73	7.0	0.0376
TR1LY1	24	11.6	0.0466
CLY5	75	17.6	0.0550
TR1LY3	34	22.4	0.0585
CLY6	78	20.0	0.0685
TR2LY4	56	27.9	0.0728
TR2LY4	54	15.5	0.0833
CLY6	76	6.5	0.1083
TR2LY4	55	20.0	0.1266
TR1LY3	32	8.5	0.1417
TR2LY1	83	25.0	0.1582
TR1LY1	23	8.0	0.1633
CLY6	79	27.5	0.1741
TR2LY1	43	32.4	0.1742
TR1LY1	27	34.3	0.2171
TR2LY1	84	9.0	0.2813
TR1LY1	25	17.0	0.3469
TR2LY1	82	12.0	0.3750
TR2LY1	42	21.0	0.4286
TR2LY4	57	53.2	0.4325
TR2LY4	53	8.5	0.5313
TR1LY3	35	37.2	1.1625

It can be seen that these data range from 0.0279 to 0.5313 ft/day unsaturated hydraulic conductivity with one case of 1.1625 ft/day. The bulk of the data fall in the lower end of the range. The high value almost certainly represents piping or

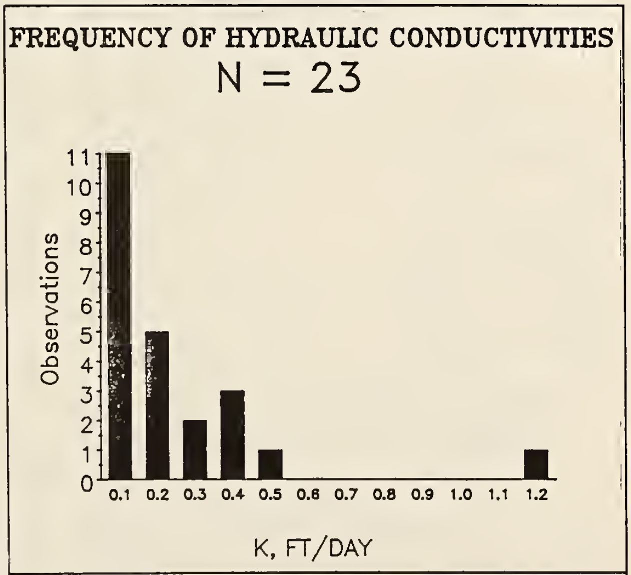

Figure 4. A frequency plot of the data from table 1.

channeling of infiltrating waters. Figure 4 is a frequency plot of the data from table 1.

Several of the lysimeters exhibited concentration peak curves which had no rising or falling limbs. That is, instead of being smoothly increasing and decreasing, the curves had step-like jump discontinuities. This can be explained as a consequence of insufficient sampling frequency for the particular peak. However, the sampling frequency was sufficiently dense to capture the concentration peak itself in all cases. In two cases an initial concentration spike was separated by a period of six months from later bromide occurrence. In the case of lysimeter 34, the two highest values, 1,161 ppb on April 14, 1987 and 1,169 ppb on August 10, 1987, are not significantly different from each other. This evidence of unsaturated fluid flow behavior is somewhat problematic. One of us (Parizek) has suggested that this may be an artifact of a dual-porosity type mechanism. Here, fluid flow might be occurring on a variety of scales: interblock flow in voids between blocks of sandstones and in voids in shaly zones, flow in finer grained matrix materials, and intrablock flow in the pores of the rocks themselves. The capillarity of finer grained matrix materials and whole rock would tend to impede flow while the interblock voids would be much more conductive. If this model is correct, then it would be possible for a lysimeter to collect waters conducted through macropores very rapidly and through micropores much later.

It is interesting to compare the values found in table 1 with those yielded from pumping tests previously conducted (Henke 1985). These saturated hydraulic conductivities ranged from about 1 ft/day in coal tipple waste composed of about 50% clay and silt-sized particles to 100 to 110 ft/day in predominantly sandstone spoil. Other values included 8 ft/day in siltstone and shale, and 55 and 60 ft/day in sandstone spoil-centered pump tests. Excluding the high and low values from table 1, the mean and median unsaturated hydraulic conductivities found at the reclaimed and revegetated mine site are 0.1876 ft/day and 0.1582 ft/day, respectively. These are between 0.14 and 18.76 percent of the saturated hydraulic conductivities.

Figure 5 is an example bromide concentration versus time plot for lysimeter 76 from Control lysimeter nest 6. The large primary peak is used for the calculation of unsaturated hydraulic conductivities. The exponential die-off curve suggests that storage capacities of the medium are not insignificant.

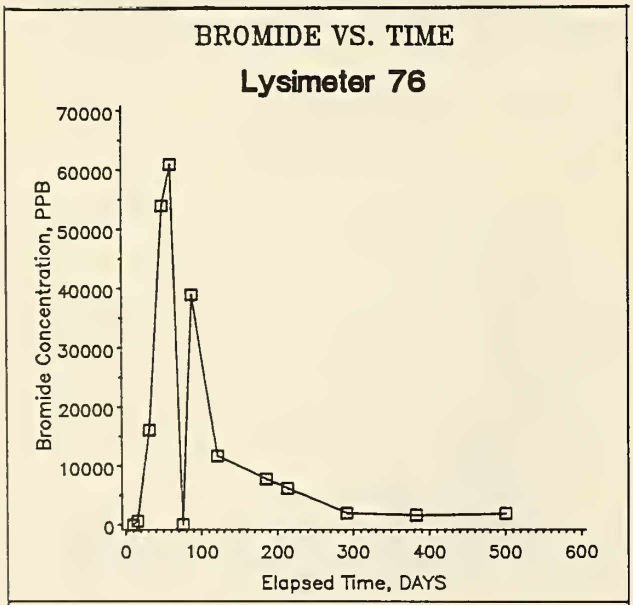

Figure 5. A plot of Br concentrations versus time for a single lysimeter. Background concentration is below detection limits (20 ppb). Application date is day zero.

Figure 6 shows the concentration values for all of the lysimeters installed in Control lysimeter nest 6. Non-ideal infiltration behavior is demonstrated here but is difficult to see because the magnitude of the concentrations varies over a wide range of values.

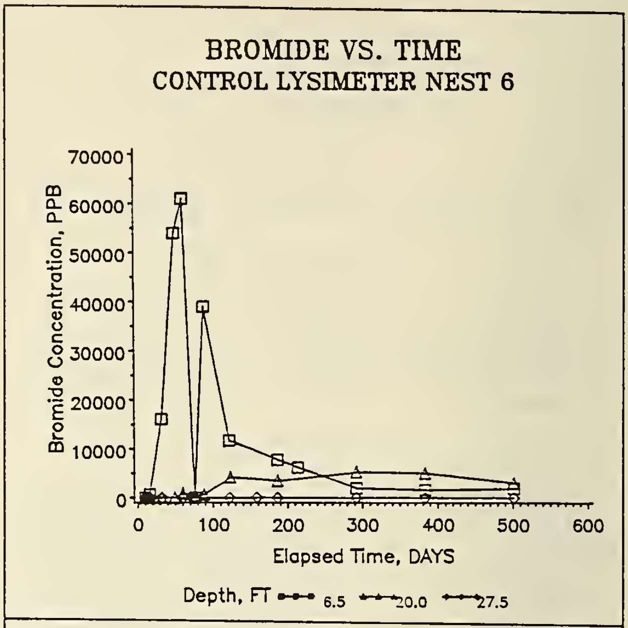

Figure 6. A plot of Br concentrations versus time. Background concentration is below detection limits (20 ppb). Application date is day zero.

For this reason the concentration peaks for each lysimeter were normalized by dividing observed concentrations by the maximum observed concentration for that lysimeter. This simplified peak identification and interpretation. An example plot of these normalized values is shown in figure 7.

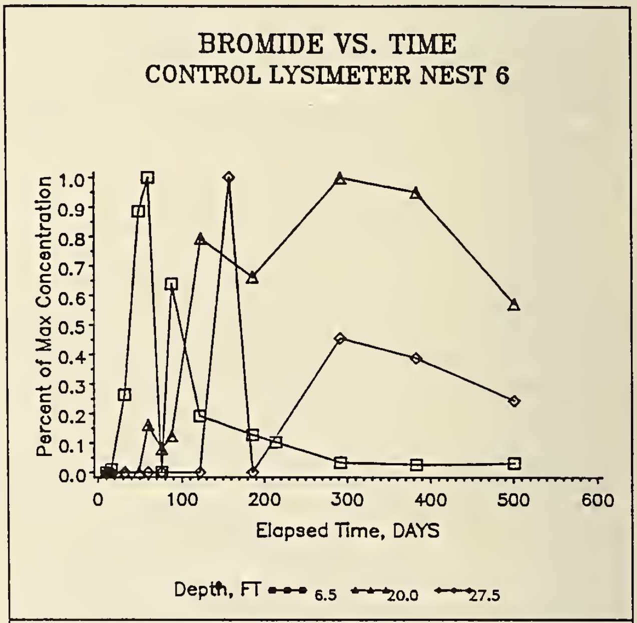

Figure 7. An example plot of normalized Br concentrations versus time. Background concentration is below detection limits (20 ppb). Application date is day zero.

Here, we can clearly see the non-ideal behavior, with the first peak in the shallow lysimeter, the second peak in the deep lysimeter, and the final peak in the intermediate depth lysimeter.

Figure 8 shows the apparent randomness with respect to depth of the hydraulic conductivities. This is consistent with the type of lithologic configurations one would expect to find in disturbed mine spoil. The vertical alignment of unsaturated hydraulic conductivities may be an artifact of insufficient sampling density, or it may be because of similarities in lithologies found at these various sampling points.

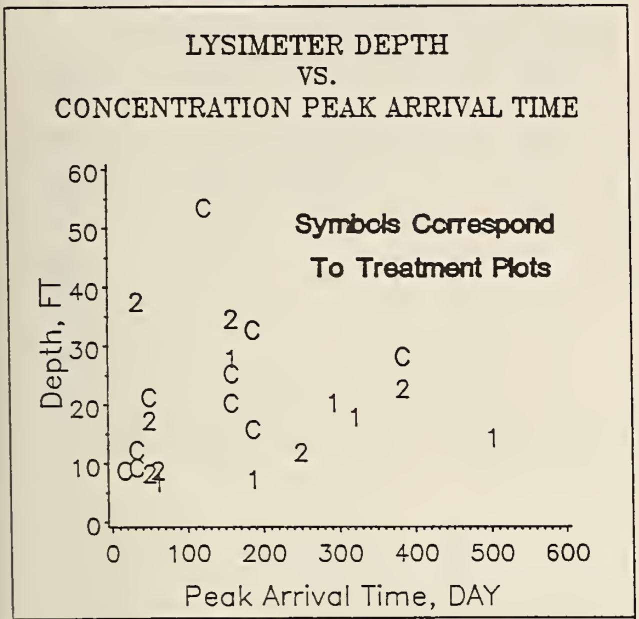

Figure 8. Scatter plot of peak arrival times vs depth. Points labelled 1, 2, and C are from treatments 1, 2, and the control plot, respectively. Rather than early peaks occurring at shallow depths, peak arrivals appear to be independent of depth. This is indicative of non-uniform, non-ideal infiltration and percolation behavior in the unsaturated zone.

With the peak arrival data in hand, and keeping in mind the assumptions previously mentioned, it is possible to calculate unsaturated hydraulic conductivity. Dividing depth by time yields the numbers depicted in figure 9, a scatter plot of depth versus unsaturated hydraulic conductivity. An examination of figure 9 suggests an irregular hydrogeologic regime, where areas of high and low hydraulic conductivity do not occur in distinct horizons, but rather are distributed more randomly with respect to depth. This insight helps us to build a more complete conceptual framework and understanding in regards to fluid flow in disturbed land.

With figures 8 and 9 in mind, table 2 is a listing of the lithologies of the lysimeter sampling points in the same order of increasing unsaturated hydraulic conductivity used in table one.

Table 2 describes a highly irregular backfill spoil pile consisting primarily of two sedimentary rock types, sandstones and shales. Perhaps more significant than the lithological descriptions in table 2 is the lack of descriptions. In many cases the log reports no return or poor return and bit drops. Furthermore, the process of backfilling sometimes required quantities of sediment many times the borehole volume to complete. All of this evidence is testimony to the frequent presence of large void spaces in the spoil pile.

ONGOING AND FUTURE STUDIES

In terms of the unsaturated fluid flow characterization, the determination of soil moisture content and bulk density are critical. Volumetric water content is the ratio of volume of water

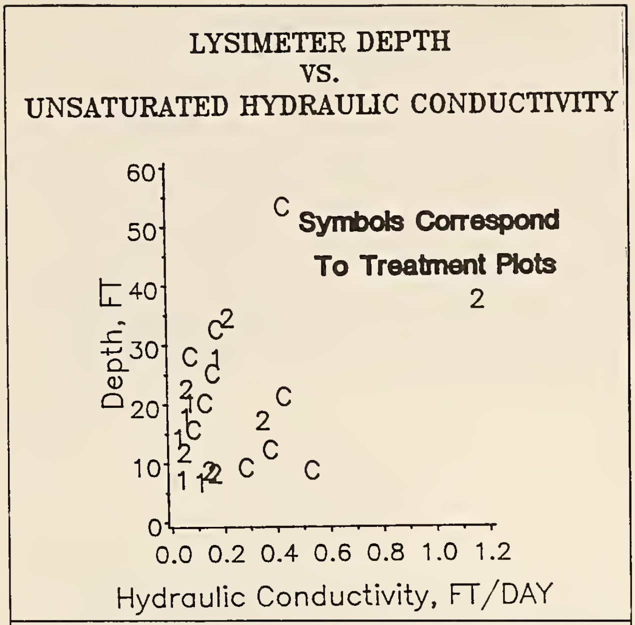

Figure 9. Scatter plot of unsaturated hydraulic conductivities versus depth. Points labelled 1, 2, and C are from treatments 1, 2, and the control plot, respectively. Randomly oriented values provide insight into the nature of fluid flow in disturbed mine spoil.

Table 2. Lithologies of the lysimeters.

Lysimeter Number	Lithology
74	Grayish-br sand and sandstone and shale/siltst frags
73	Grayish-br sand and sandstone and shale/siltst frags
24	Orangish-br sand and sandstone frags
75	Grayish-br sand and sandstone and shale/siltst frags
34	Poor return, bit drop@10 ft, boulder@27 ft
78	Poor return, gray to yellowish-br sand and sandstone frags, some coal frags
56	No return, bit dropped 0.5 ft@5,15 and 20 ft
54	No return, bit dropped 0.5 ft@5,15 and 20 ft
76	Gray to yellowish-br sand and sandstone frags, some dark-gray shale/siltstone and coal frags
55	No return, bit dropped 0.5 ft@5,15 and 20 ft
32	Gray to brownish-gray sandstone fragments
83	Poor return, gray sand and sandstone frags and dark-gray shale frags
23	Gray sandstone frags and yellowish-br sand
79	No return
43	Poor return, gray sand and sandstone frags and dark-gray shale frags
27	Poor return, br sand and sandstone frags
84	Poor return, gray sand and sandstone frags and dark-gray shale frags
25	Orangish-br sand and sandstone frags
82	Poor return, gray sand and sandstone frags and dark-gray shale frags
42	Poor return, gray sand and sandstone frags and dark-gray shale frags
57	No return, bit dropped 0.5 ft@5,15 and 20 ft
53	No return, bit dropped 0.5 ft@5,15 and 20 ft
35	Poor return, bit drop@10 ft, boulder@27 ft

to total volume, while bulk density is the ratio of dry mass of solid to total mass (Fritton 1986). Recalling that unsaturated hydraulic conductivity is a function of volumetric moisture content, this parameter is of interest. Knowing volumetric moisture content and bulk density, total porosity of the conducting medium can be calculated. An understanding of total porosity and bulk density will help to gain insight into the nature of the matric materials and their arrangement, which have a large influence on matric potential. Although the tracer study has been underway for some time, it is still desirable to obtain some representative values for soil moisture content under different meteorological conditions. This enhancement of the breadth and scope of the unsaturated fluid flow characterization of mine spoil is the motivation for the depth-density and depth-moisture profiling that is in progress. The specific relation between bulk density, total porosity, and volumetric moisture content is

$$E = 1 - (\theta_v \rho_w / \rho_s - \rho_t / \rho_s) \quad (3)$$

where

E = Total Porosity

ρ_t = Bulk Density, M_t/V_t

θ_v = Volumetric Water Content, V_w/V_t

The values for θ_v and ρ_t can be empirically determined from *in situ* investigations using depth-moisture and depth-density neutron thermalization probes. ρ_w is taken to be 1.0 g/cm^3 and ρ_s is taken to be 2.65 g/cm^3. This derivation is based on the relations of Fritton (1986).

With the goal of depth-moisture and depth-density profiling in mind, six 20 ft-long very thin walled (0.035 in.) seamless aluminum access tubes were installed at the site in early September 1987. The installation locations were chosen to investigate the several characteristic heterogeneities and anisotropies found at the site. Further, the access tubes were installed proximal to the lysimeter nests whose flow behavior has been investigated in detail through large numbers of neutron activation analyses. With this strategy, a more definitive and detailed understanding of the fluid flow behavior at the site may be realized.

In addition, we recognize that sampling schedules may produce artificially skewed concentration peak dates and thus alter calculated unsaturated hydraulic conductivity. In the light of this, a remedial solution may be found in geostatistical approaches. That is, the determination of a semivariogram containing the concentration values at the sampling point through time may yield somewhat different peak dates.

CONCLUSIONS

A tracer study using non-radioactive neutron activatable bromide-79 was employed as an investigative technique to determine *in situ* unsaturated hydraulic conductivities in a reclaimed and revegetated strip mine. Subsequent to the application, water samples were collected through time from 55 of the pressure-suction lysimeters installed at various depths at the field area. 23 were selected for study and neutron activation analysis was used to determine Br concentration. Interpretation of the concentration peaks as average arrival times of infiltrating rainwater yielded unsaturated hydraulic conductivities ranging from 0.0279 to 0.5313 ft/day with one value of 1.1625 ft/day. This high value is interpreted as an example of infiltrating water piping through the highly heterogeneous disturbed spoil pile. Excluding the high and low values, the mean and the median unsaturated hydraulic conductivities were found to be 0.1876 ft/day and 0.1582 ft/day, respectively. These values are in the range of 0.14 to 18.76 percent of saturated hydraulic conductivity of the various geologic materials at the site.

The spoil at the site is composed of blocky, often micaceous, sandstones and finer grained disaggregated shales. The presence of many void spaces in these disturbed sediments is suggested both by the lithologic logs of the drill holes and by the difficult experience backfilling some of these same holes, which often required many times the borehole volume to complete. Despite these void spaces, only one suspected case of chanelling was found. Consistent with other undisturbed environments, in the disturbed mine spoil unsaturated hydraulic conductivity is one to three orders of magnitude less than saturated hydraulic conductivity. The values calculated have a narrow range and appear to be largely independent of localized lithologic heterogeneities. This, however, may be an artifact of a sketchy drill log record. Accurate and complete drill logs from disturbed mine spoil materials continue to prove difficult to obtain, as cuttings are often lost to the subsurface voids. With these unsaturated hydraulic conductivity values in hand, it is possible to calculate volumetric and mass flux of percolating waters through a unit cross-sectional area under a unit hydraulic gradient. Given an estimate of alkaline load in percolating soil water, either empirical or theoretical, it is possible to calculate acid neutralization potentials for a given mass or volume of water. Comparing these figures with acid production estimates should yield valuable insight into the effectiveness of a given surficial application of alkaline material. Clearly, the dramatic loss of hydraulic conductivity under unsaturated conditions presents a significant retardation factor in the speed and effectiveness of *in situ* abatement efforts.

Further refinement of the data may be yielded by geostatistical investigations, as the semivariogram of the concentration values at a sampling point through time may suggest alternative concentration peak dates. A second investigative technique, the use of neutron depth-density and depth-moisture probes, will be of use in the determination of soil bulk density and soil moisture content values. These data will help to quantify the range of unsaturation under which these spoil waters moved.

The abatement of acid mine drainage from strip mines through the use of surficial applications of lime plant flue dust and limestone quarry waste depends heavily on alkaline-charged waters percolating through acid-producing spoil material. Thus, an increased understanding of the behavior and transport rates of water through the unsaturated zone is of great value. With the unsaturated hydraulic conductivity values yielded from this study, investigators will be better prepared to evaluate past abatement strategies and plan future abatement strategies.

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FORECASTING THE EFFECT OF MINE SITE REHABILITATION WORKS ON LOCAL GROUND WATER QUALITY[1]

David K. Gibson and Garry Pantelis[2]

Abstract.--A large rehabilitation project has been carried out on an abandoned uranium mine at Rum Jungle in the Northern Territory of Australia where oxidation of pyritic mine wastes has led to substantial water pollution. This pyritic oxidation has been halted by the exclusion of air and water from two rock heaps by contouring and installing a clay cap. Ground water levels and quality have been monitored for acidity and dissolved metals over the four years since the project began. Although the contaminant input to the local river has dropped markedly, there has been no significant change in ground water quality. The purpose of this work is to estimate the time scale over which an improvement might be expected to occur. A model in which the main store of pollutant is assumed to be the contaminated water below the heap leads to the very low estimate of less than four years. A more complex model which accounts for contaminants stored in pore water held within the dump produces an estimate, so far consistent with observation, of 20 years. The possibility of heavy metals being stored in the form of a buffered precipitate cannot be excluded. Thus, the importance of continuing the monitoring of the site is emphasised.

INTRODUCTION

Rum Jungle is on the East Finniss River, about 70 km south of Darwin in the Northern Territory of Australia. From 1954 to 1971 it was the site of a mining operations where uranium and copper were extracted by opencut mining. The East Finniss River was significantly contaminated by heavy metals during mining, and this continued after the mine was abandoned. The mean concentrations of the metals in the river were a few mg/l, but owing to the strong seasonal variation in the rainfall, the actual concentrations varied widely, being rather high at the periods of small flow at the beginning and end of the wet season. The average rainfall is about 1.5 m/y falling mainly in a wet season over the period October to April.

During the 1970s the environmental problems of the site were investigated to elucidate the nature of pollution caused by mining. It was demonstrated that most of the heavy metal pollution arose from three large overburden dumps (one of 7 million tonnes and two of 2 million tonnes) and a heap leach pile, in which pyrite was oxidising, catalysed by bacteriological activity (Harries and Ritchie 1987). Heavy metals in the pyritic rock were solubilised in this process and were eventually transported by water movement into the river system.

The rehabilitation works were carried out from 1983 to 1985. The tailings were disposed of in one of the three opencut pits. The water in the other two pits was treated, the pH being raised from about 3.5 to 7.5, with consequent precipitation of the dissolved heavy metals. The tops of the waste rock heaps were contoured and capped with layers of clay, loam, and sandy gravel with total thickness of about 600 mm (Northern Territory Department of Mines and Energy 1986(a)). The dumps were vegetated with a mixture of grasses and legumes, and erosion was controlled with a system of bunds and rock drains. The sides of the heaps were sloped at a maximum of 1 in 3 and faced with rock.

The clay cover was designed to reduce the infiltration of water through the heaps. Measurements with collection lysimeters have shown that the infiltration of rain water has been reduced to less than 10% of its former value. Measurements of the oxygen levels and heat generation in the dumps have shown the pyritic oxidation has also been greatly reduced (Harries and Ritchie 1987). Two overburden heaps were selected for intensive study. The ground water in their vicinity was monitored by about 30 boreholes for the purpose of estimating the rate at which the quality of the ground and surface water could be expected to improve over the coming years following the cessation of pollutant generation.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference, sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), Pittsburgh, Pa, April 17-22, 1988.

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MODEL OF POLLUTANT RELEASE FROM BELOW WASTE ROCK HEAP

Estimated pollutant release was based on a simple two-dimensional model applied to the White's heap, the largest waste rock heap. This heap extends for about 600 m along a gently sloping ridge. It is about 20 m high and 600 m wide. The ridge continues for some 200 m upslope of the dump to a water divide at the top of the hill. The underlying ridge has a permeable layer of soil about 2 m thick sitting on fairly impermeable rock. This is shown in schematic form in figure 1, in which the x-axis coincides with the fall of the ridge.

The water in the aquifer below the dump is a reservoir of dissolved heavy metals, generated before the clay cap was installed. This contaminated water will be flushed out as rainfall recharges the aquifer upslope of the heap. An estimate of the time taken for this flushing process should provide a lower bound for the time before any improvement in ground water quality can be expected as other processes, such as the flushing of contaminated water stored in the unsaturated zone in the dump itself, will add to this time.

Assuming steady-state conditions, we can calculate a water table height by using the Dupuit-Forscheimer equation (Bear 1972). If the phreatic surface is represented by $\phi(x)$, the base of the aquifer by g(x), the saturated hydraulic conductivity by K_s, and the total horizontal discharge by q, we have

$$\frac{dq}{dx}=-\frac{d}{dx}\left[K_s(\phi-g)\frac{d\phi}{dx}\right]=0, \qquad 0<x<L \qquad (1)$$

At x = 0 we have the boundary condition

$$q=-(\phi-g)K_s\frac{d\phi}{dx}=Q \qquad (2)$$

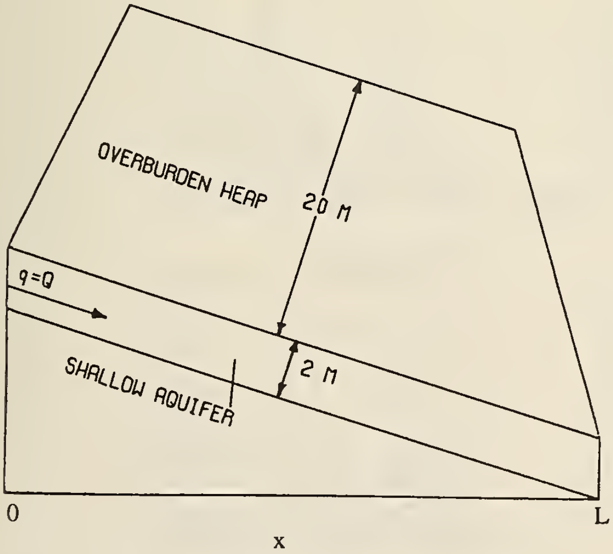

Figure 1.--Schematic diagram of mine waste overburden heap lying on sloping ridge. The vertical scale is greatly exaggerated.

where Q is the recharge from the upslope aquifer. From (1) and (2) we simply have for steady conditions

$$q(x)=Q \qquad 0\leqslant x<L \qquad (3)$$

If we take the convection-dispersive equation (CDE) for one dimensional saturated horizontal flow, assume uniform vertical concentration and ignore dispersion, we have

$$\theta_s\frac{\partial c}{\partial t}+\frac{q}{h}\frac{\partial c}{\partial x}=0 \qquad (4)$$

where h = ϕ-g, θ_s is the saturated moisture content of the aquifer and c is the contaminant concentration. Under pure advection the fresh water/contaminated water interface is given by the characteristic curve of (4), which is

$$\frac{dx}{dt}=\frac{q}{\theta_s h}=\frac{Q}{\theta_s h} \qquad (5)$$

emanating from x = 0 at time t = 0.

Since h is a function of x we may invert (5) and solve for t as a function of x, i.e.

$$\frac{dt(x)}{dx}=\frac{\theta_s h(x)}{Q} \qquad (6)$$

The travel time, t_0, for contaminants starting at x = 0 (t=0) and reaching x=L is obtained from

$$t_0=\frac{\theta_s}{Q}\int_0^L h(x)dx \qquad (7)$$

Noting that here 0 <h(x) ≤ 2m we have

$$0<t_o\leqslant\frac{2\theta_s L}{Q} \qquad (8)$$

An estimated value of Q is given by the product of the length of the recharge region (200 m), the annual rainfall (1.5 m/y) and the infiltration coefficient (0.5). Thus Q = 150 m^2/y and an estimate of θ_s = 0.4 were used to yield the estimate of 0 < t_o ≤ 3.2 years for the flushing-out period.

A more elaborate model has also been used for this problem, in which the flushing of the unsaturated moisture from the heap was included (Pantelis 1987). A vertical averaging procedure was used to deal with the contaminant profile. In order to avoid making the assumption of uniform vertical concentration in the CDE the product of moisture content and contaminant concentration, θc, was replaced by its vertical average. This somewhat artificial manipulation introduced the vertical integral of θc as the dependent variable. This approach implies a more vertical uniformity of contaminant mass rather than of concentration, which may be more realistic since, in the absence of recharge at the top of the overburden heaps, low moisture contents and low mobility of contaminants could result in higher concentrations existing there. A high concentration of contaminants in the pore water in the upper levels of the dump is supported by measurements made on samples taken from the heap (Goodman *et al.* 1981). However, this assumption, together with the low percentage of rainfall infiltrating the clay capping, could lead to an overestimate of the flushing time. A period of 20 years was evaluated by this model, which, for the above reasons, must be taken as an upper limit. It is stressed that the flushing time could be longer if heavy metals continue to be mobilised, for instance by the remobilisation of metals deposited as minerals during the period of pyritic oxidation.

FIELD MEASUREMENTS

Around the time of the capping of White's heap about 20 boreholes were drilled into the aquifer at various points about the perimeter of the heap; one hole was drilled through the heap into the aquifer below. These have been monitored for water level, pH, electrical conductivity, and concentrations of copper, zinc, manganese and sulphate, approximately at monthly intervals, from the end of 1983 till the present. Results for a typical borehole near the perimeter of the heap and for the borehole through the heap are shown in figures 2 and 3. Estimates of the total annual contaminant loads in the Finniss River have also been made (Northern Territory Department of Mines and Energy, 1986(b)) and are shown in table 1.

As can be seen from figure 2, the ground water quality has not changed significantly over the four years since rehabilitation. It would take considerable stretching of the parameter values used in the simple model to achieve consistency with this time. It is therefore evident that there is a store of contaminants additional to that in the ground water. The 20-year period estimated using our second model, which accounts for the storage of contaminants in pore water held in the dump, is consistent with the data, as is the prediction that no change is expected for the period, after which change is rapid. However, it cannot as yet be demonstrated whether this store is the controlling factor or whether the contaminants are stored in the form of a buffered precipitate.

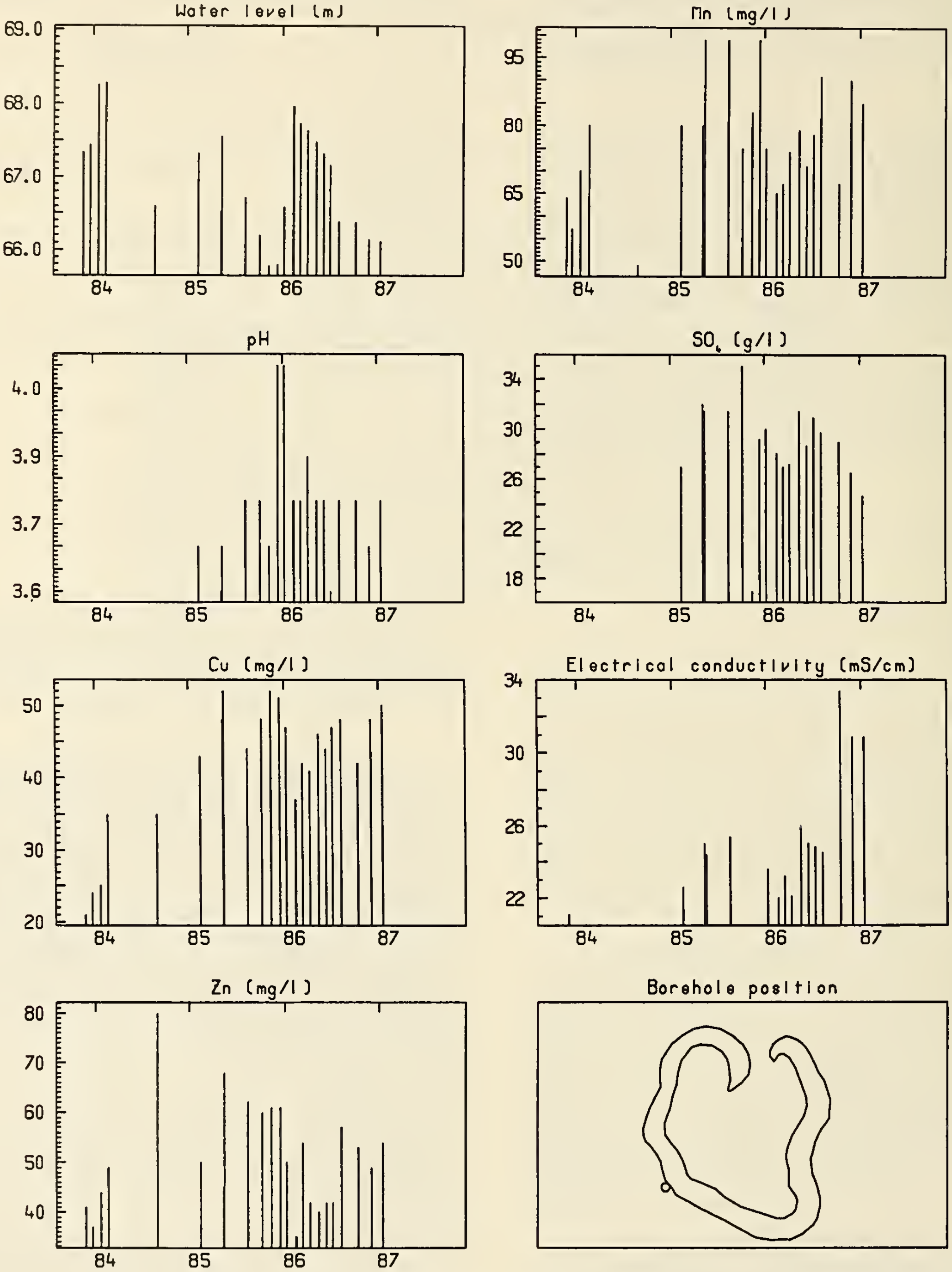

Figure 2.--Data from borehole No. 22084 from 1984 to 1987.

It is interesting to note the seasonal variation of water level and contaminant concentration observed beneath the heap and shown in figure 3. There is obviously considerable water movement below the dump. It also appears that the contaminant concentrations fall during the wet season, due to dilution by fresh water, and then rise during the dry. This could be due to the redissolving of precipitates or to input from the concentrated pore water.

Table 1 shows that the total input of heavy metals to the river system has fallen markedly. Again this is consistent with the prediction of the more complex model that the total discharge of pollutants from waste rock dumps will decrease after capping, because of reduced water discharge.

CONCLUSIONS

The field measurements show that it takes at least four years before ground water quality in the vicinity of a large overburden rock dump will respond to measures that stop leaching of heavy metals from it. We have shown that this period cannot be accounted for on the assumption that the main store of contaminants is in the ground water below the dump. It is, however, consistent with a more complicated model in which contaminants are assumed to be held in concentrated solution in the pore water held in the rock heap. As the system under investigation is a major rehabilitation work and has been well monitored from the outset, it is most important that monitoring continue until the trend in ground water quality becomes clear.

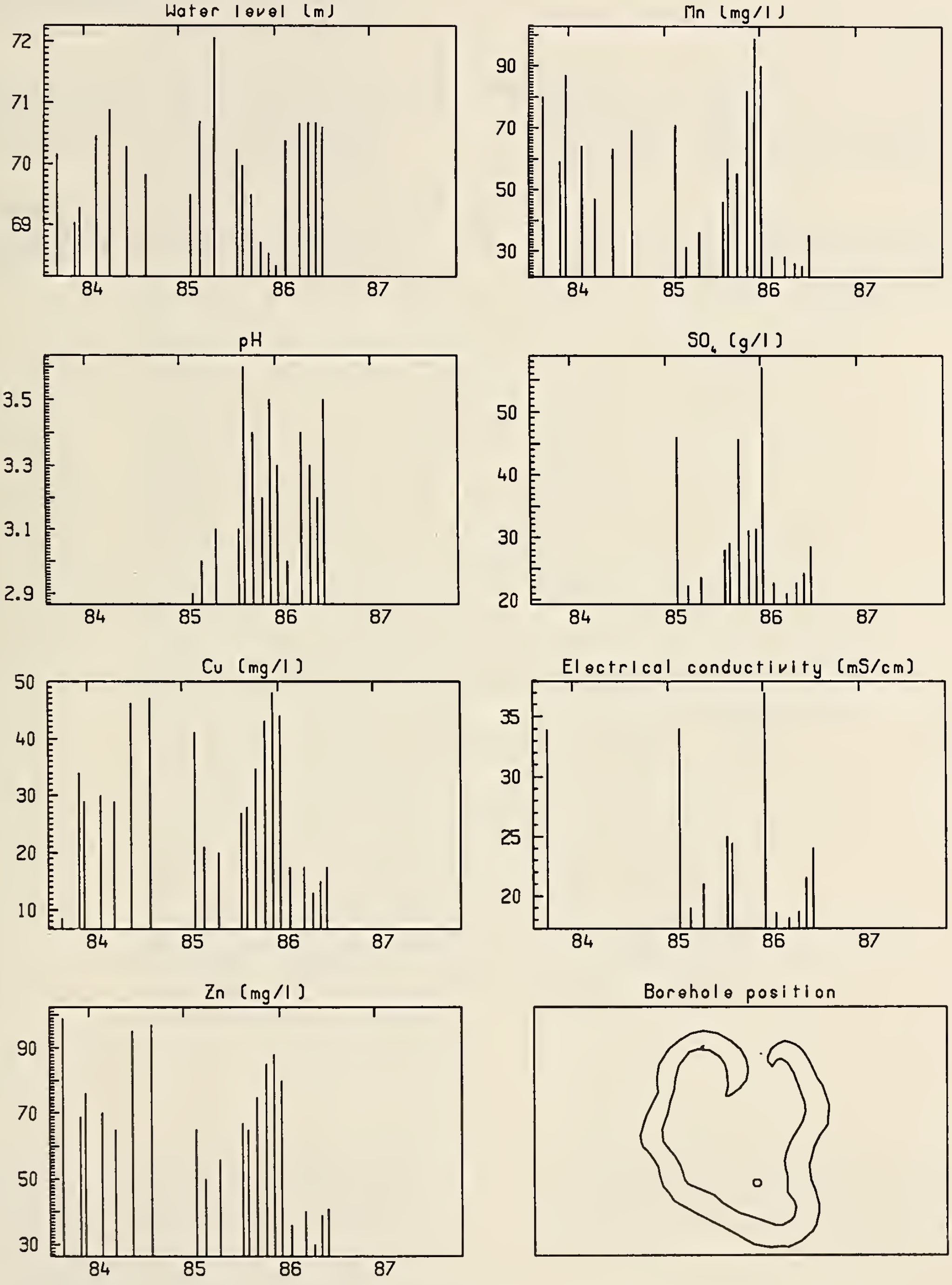

Figure 3.--Data from borehole No. 22082 from 1984 to 1987.

Table 1.--Summary of monitoring results for the East Branch of the Finniss River.

Season	1982/83	1983/84	1984/85	1985/86
Rainfall (mm)	1121	1704	1112	910
Total flow ($m^3 x 10^6$)	9.5	48	11.7	11.4
Metal load (t) Copper	23	28	9	4
Manganese	5	9	4	3
Zinc	5	9	4	3

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PHOTO-LINEAR CHARACTERIZATION, LITHOLOGIC VARIABILITY, AND THE EFFECTS OF MINING ACTIVITY BY FRACTURE STUDIES AND IN SITU, AIR-INJECTION, PERMEABILITY TESTING[1]

Christopher A. Shuman and Richard R. Parizek[2]

ABSTRACT

Highwall fracture studies and a novel permeability testing technique were used in a study of the subsurface character of a photo-linear "fracture trace". This study focused on a topographic-tonal, photo-linear feature that intersected the highwall of an active surface coal mine working the Freeport-Mahoning coals near Clearfield. Aerial photographs at 1:12,000 scale were used for the photo-linear analysis, and critical features were examined in the field. Fracture data on joints and faults were gathered in traverses along highwall exposures of a relatively uniform siltstone unit overlying the Upper Freeport Coal, and hydrologic tests through borehole packers were conducted in overburden shotholes and selected monitoring boreholes drilled into the siltstone. The orientation of photo-linear and joint distribution maximas compare well, both falling between 320 - 340 degrees. Joint frequency analysis indicated that fracturing increased slightly near the photo-linear feature's subsurface projection. However, the correlation of this feature with a swale in the Mahoning Coal (possibly an old distributary channel) indicated that fracture frequency increases are probably related to stratigraphic phenomena rather than "fracture traces". The air-based packer test technique used for the permeability testing was designed to gather data rapidly from available boreholes, especially those in unsaturated units adjacent to the mine pit. A total of 55 permeability values were obtained from the siltstone. These values defined the permeability variation within the siltstone (probably 1.0 to 7.0×10^{-13} ft^2), evaluated the effect of mining activity on bedrock permeability (2x + increases extending 20-30 ft from the highwall), and enabled the air-permeability values to be correlated with the hydraulic conductivity values (3.9 to 5.1×10^{-7} ft/sec) derived from water-based tests. In addition, air-injection test factors (such as Klinkenberg slippage, partial saturation, and turbulent flow) and some additional uses of the technique were given a preliminary evaluation.

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[1] Paper given at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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INTRODUCTION

One topic which has recently received more than passing attention from hydrogeologists is the movement of ground water through subsurface fractures. This interest is due to the ubiquitous nature of geologic fractures, their generally permeable character, and the fact that they can interfere with the application of Darcy's Law. By studying the nature of fracture flow, as well as the distribution and character of fracture features, ground-water scientists can better adapt porous media theory, based on Darcy's Law, to fit particular geologic situations. This will improve understanding and prediction of ground-water flow in many geologic systems. However, a great deal of information on the subsurface nature of fracture features and their effects on porous media must be gathered before consistent evaluation of these systems will be generally possible.

The primary objective of this study was a quantified evaluation of the geologic and hydrologic character of the subsurface expression of a photo-linear "fracture trace" feature. Because these features have been correlated with zones of weakness and increased ground-water flow (Lattman and Matzke 1961, Parizek 1976), it was expected that this research would yield valuable field data on the nature of these features that could be applied in other areas. This was to be achieved by fracture studies and in situ permeability tests that could be focused where a mapped feature intersected the highwall of a surface coal "strip" mine. Secondary objectives to be studied included the variability of permeability within a fractured lithology, the effects of mining on permeability, and the factors affecting the field use of air-injection permeability tests.

This study was conducted in Clearfield County in the Appalachian Plateau region of Pennsylvania. The Browncrest III surface coal mine, operated by the Central Pennsylvania Coal Company of Clearfield, was selected as the study site because of the availability of recent aerial photograph coverage of the mine, the presence of a photo-linear feature that intersected the mine pit, the relatively uniform and undisturbed nature of the exposed lithologies, as well as the cooperative attitude of the mine operator.

RESEARCH TECHNIQUE

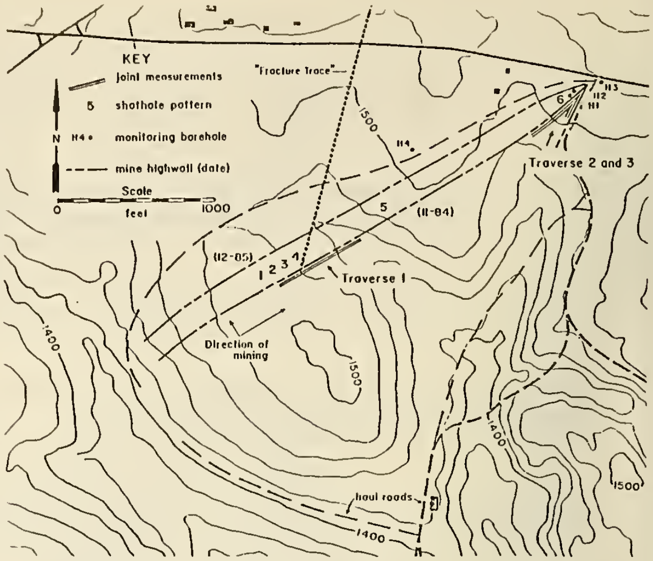
KEY
joint measurements
"Fracture Trace"
5 shothole pattern
N H4• monitoring borehole
mine highwall (date)
Scale
0
feet
1000
1500
H4
H3
H2
H1
6
Traverse 2 and 3
5
(11-84)
(12-05)
1 2 3 4
Traverse 1
Direction of mining
1400
1500
1400
1500
haul roads
1400

Figure 1 -- Location map of study area features.

As illustrated by figure 1, the research technique employed in this study had three phases: 1) identification of a photo-linear fracture trace feature where it crossed a mine highwall, 2) measurement of joints and faults in traverses of a suitable highwall lithology near the fracture trace and in other areas of the pit, and 3) development and application of the permeability testing technique in available overburden shotholes and monitoring boreholes drilled in the vicinity of the feature. By examination of the exposed lithologies (from the Lower Freeport Coal to a sandstone above the Mahoning Coal), it was decided to concentrate the fracture studies and hydrologic testing on a siltstone unit that overlies the Upper Freeport coal (see figure 2). This unit was selected because of the number of drillholes into it, as well as its consistent character and exposure across the mine.

Photo-linear Fracture Trace Analysis

The fracture trace analysis was done in order to characterize the overall distribution of photo-linear features and to provide a basis for comparision with other available data on joints and fracture traces for this region. The technique used to map the photo-linear fracture trace features at the mine site

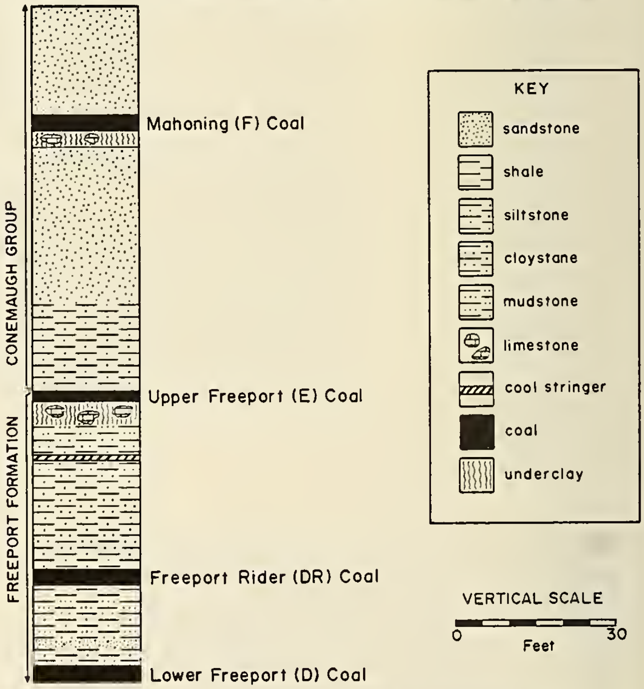
Mahoning (F) Coal
CONEMAUGH GROUP
Upper Freeport (E) Coal
FREEPORT FORMATION
Freeport Rider (DR) Coal
Lower Freeport (D) Coal
KEY
sandstone
shale
siltstone
claystone
mudstone
limestone
coal stringer
coal
underclay
VERTICAL SCALE
0
Feet
30

Figure 2 -- Composite stratigraphic section for the study area.

was derived from Lattman (1958) and Meiser and Earl (1982). Aerial photographs at 1:12,000 scale were studied individually and in stereo with the aid of a mirror stereoscope. The ends of observed features were marked on acetate overlays and the fracture trace feature shown in figure 1 was then field-checked for accuracy. Previous mining activity to the south and east of the mine pit made the analysis difficult. However, the three images which provided the photographic base for this analysis were of excellent quality, revealed land surface details with great clarity, and were only a few months old when this study began.

Highwall Fracture Studies

In order to determine if the photo-linear fracture trace feature intersecting the mine pit was related to a subsurface zone of fracture concentration, highwall fracture studies were conducted. The objective of this phase of the research was a qualitative and quantitative evaluation of joints and other geologic fractures that could be observed in highwall traverses. Joint measurements were made in 3 traverses, in the vicinity of the mapped feature as well as in areas thought not to be affected by linear features. Joint and fault planes were distinguished from blasting related fractures on the basis of their extent, regularity, degree of weathering, and relationship to remanents of shotholes visible along the highwall. The mapped joint and fault features were located along the 3 traverses with a fiberglass measuring tape. A Brunton compass, scale, and set of descriptive criteria were used to characterize each joint or fault identified along a traverse.

Air-Injection Permeability Testing

In order to conduct the density of permeability tests necessary to quantify the subsurface nature of the mapped photo-linear fracture trace, a novel air-injection permeability measurement technique had to be developed. This technique, illustrated in figure 3, was designed to quickly and accurately gather bedrock permeability values from test intervals at the bottom of overburden shotholes drilled in the siltstone. By testing in the patterns of these shotholes (closely spaced boreholes with similar characteristics), information on the spatial variation and factors affecting in situ permeability determinations was gathered.

Due to the nature of the surface mine environment, the technique had to be mobile, durable, and designed to operate in unsaturated conditions. The equipment item which made this possible was the borehole packer. By using a single packer to isolate the bottom of the borehole, permeability values were obtained from the constant-head (steady-state) air-pressure and corresponding air-flow conditions that could be developed in each test interval. These air tests were patterned on constant-head water tests used to gather hydraulic conductivity data under saturated conditions (Houlsby 1976).

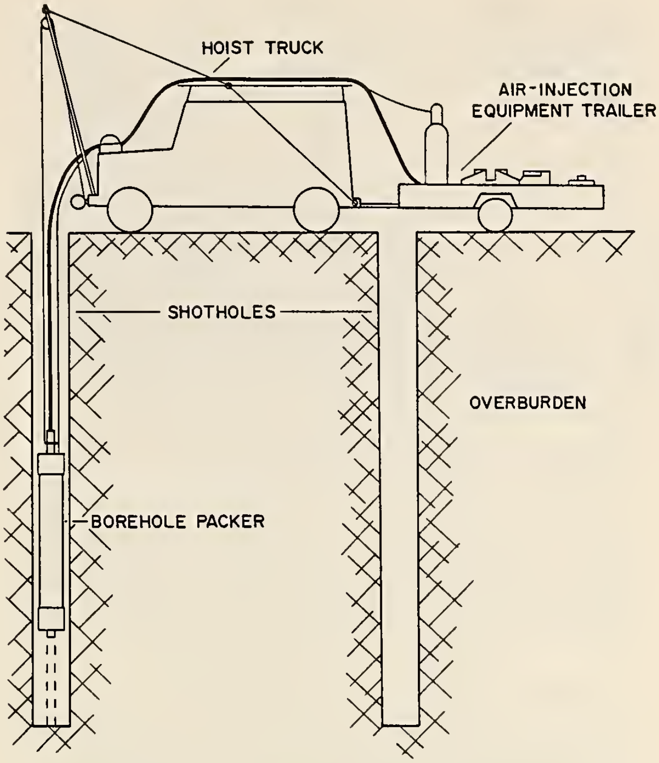

Figure 3 -- Schematic of air-injection permeability test.

Because of the severe limits on testing time imposed by the active mining, as well as equipment and manpower restrictions, it was not possible to gather subsurface fracture data from tested intervals with an impression packer.

The standard testing format, following insertion and inflation of the single packer, was a multiple step (abcba) test conducted in a sequence of pressures of approximately 10, 20, 30, 20, and 10 lb/in^2 (psi). For each injection pressure step, a flow rate in ft^3/min (cfm) was recorded. Following completion of the last pressure step, the packer was deflated, withdrawn, and the testing apparatus was moved to the next shothole. All data were analyzed by the equation:

$$k=[uQ/[2nh(P_w-P_a)]]\ \ln(r_e/r_w)$$

where k is material permeability, u is dynamic viscosity, Q is fluid flow rate, n is pi, h is tested length of borehole, Pw is average borehole pressure, Pa is atmospheric pressure, r_e is the effective borehole radius, and r_w is the actual borehole radius (Blankenship and Stickney 1983). The multiple-pressure step method was designed to yield data on the behavior of test factors such as Klinkenberg slippage, turbulent flow, partial saturation, and other complicating factors (Klinkenberg 1941, Pearson and Money 1977).

The tests were usually run in the overburden shotholes (20 to 40 holes in a pattern) in the time between drilling and detonation. This restriction prevented all retesting of the boreholes as well as borehole development. However, the method proved capable of providing numerous permeability values from the siltstone unit (average borehole spacing of approximately 15 ft). Other tests were conducted in monitoring boreholes outside the immediate mining area. Unfortunately, these holes were not as close to the mine highwall and were partially saturated with water which made them unsuitable for air-testing. They were suitable for the more traditional hydrologic tests which were conducted as a check of the air-injection technique's accuracy.

Other Hydrologic Tests

In order to obtain hydraulic conductivity values from the siltstone unit which could then be compared to the air-based permeability data, both falling-head (slug) and constant-head (steady-state) water injection tests, using standard methods and analysis routines, were conducted in the available monitoring boreholes (Fetter 1980, Cooper et al 1967, Price et al 1982). These boreholes served as the site for tests of other applications of the air-injection system, such as falling-head air-injection tests and air-injection interference tests between adjacent boreholes.

RESULTS AND DISCUSSION

Photo-Linear Fracture Trace Analysis

The results of this phase of the research are presented in figure 4 which shows the orientation diagram for the 24 features observed in the vicinity of the mine site. These features showed a broad orientation maxima between 300 and 340 degrees of azimuth with a peak between 320 and 330 degrees. The features ranged in length from 2,000 to 5,500 ft and were defined by alignments of topographic, tonal, and or vegetative features. The photo-linear feature of interest to this study was identified by a combination alignment of topographic and tonal elements trending to the northeast of the mine. The orientation results compare well to other published results (Lattman and Nickelsen 1958) and the distinct orientation of several local tributary streams.

Highwall Fracture Studies

Prior to the fracture mapping of traverses along the siltstone unit, an anomalous zone was identified between the Lower Freeport and Upper Freeport Coals. As this zone was in close proximity to the surface swale which defined the topographic element of the photo-linear feature of interest, it was initially thought to be the subsurface expression of the photo-linear fracture trace. However, closer examination of the zone revealed several vein-like clastic infillings similar in character to the local underclay and that the zone was offset to the east of the photo-linear feature. Other areas of the mine contained concentrations of these "clay vein" structures which were also not apparently related to fracture trace features.

The three traverses of the siltstone unit also provided information on the fractures related to the mapped photo-linear feature as well as on the general distribution of joints in the area. In a total of 1,200 ft of highwall, 360 joints were identified. These features revealed a dominant orientation maximum between 320 and 340 degrees (figure 5) which compares well with the orientation data provided by the previous analysis as well as other published joint surveys. Although there is variation between the three traverses, the orientation data are dominated by this distinct peak. It should be noted that the highwall was controlled by a face joint set which had a trend at approximately 90 degrees to the joint orientation maxima. The joint data is biased, therefore, because traverses along the highwall were much more likely to observe face perpendicular joints than face parallel joints.

The joint data were also examined by preparing histograms of the number of joints per traverse interval (figure 6). This graphical technique revealed a peak to the east of the intersection point between the highwall and the mapped photo-linear feature. The number of joints per 20 ft traverse interval ranged from 2 to 11 with a mean of 6. This compares well to data for joint frequency in shales included in Nickelsen and Hough (1967). The peaks in figure 5 are not thought to be related to distinct fracture zones; rather they appear to be related to stratigraphic features like the ones previously noted.

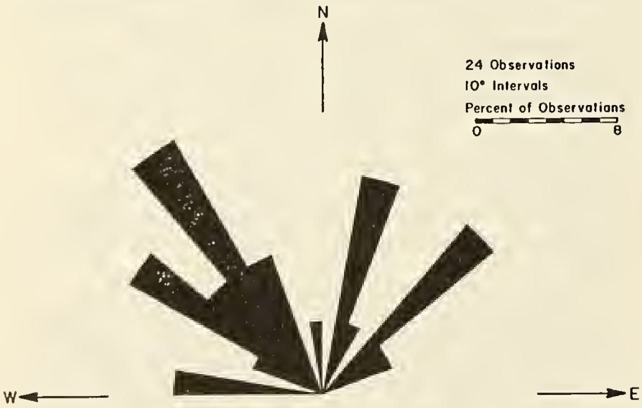

Figure 4 -- Orientation rose of photo-linear fracture trace features.

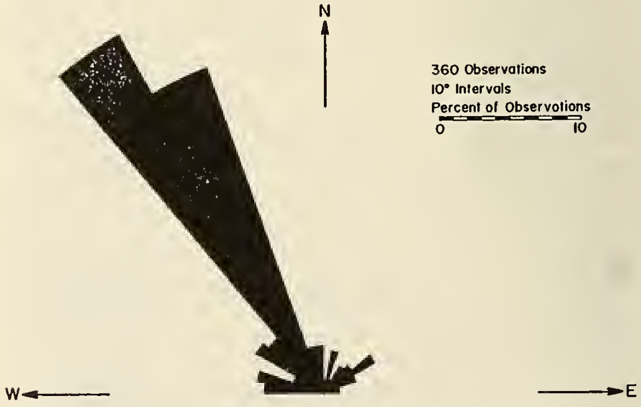

Figure 5 -- Orientation rose of all joint data.

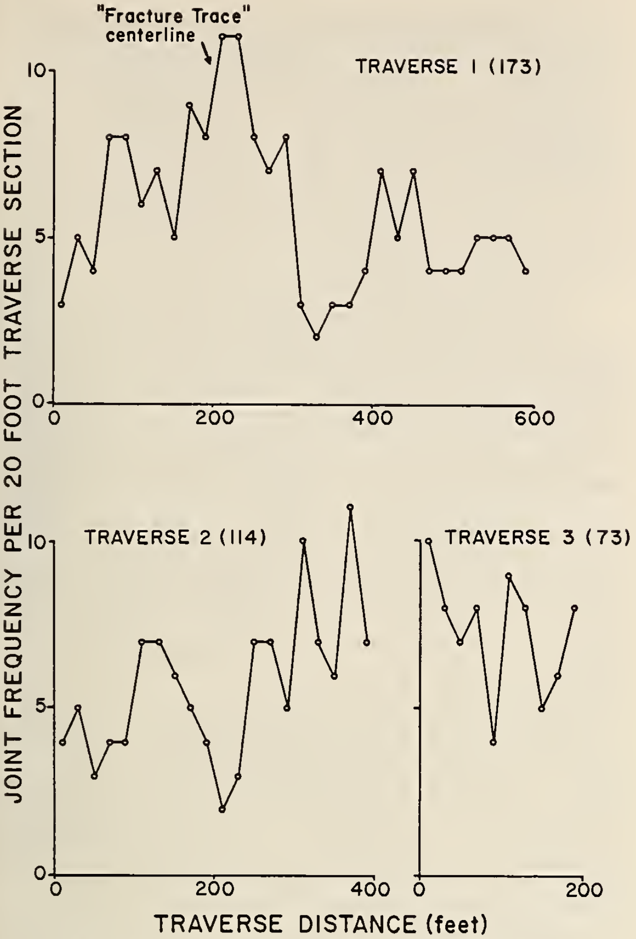

Figure 6 -- Traverse joint frequency distributions.

Air-Injection Permeability Testing

Because these air-injection tests make up the bulk of the quantitative data that was collected in this study, their analysis was critical to the objectives of this project. A total of 55 air-injection tests were conducted in six patterns of shotholes drilled into the siltstone unit. This particular aspect of the study gained importance with the discovery, by visual inspection of the highwall during the testing of Shothole Pattern 4 (see figure 1), that the photo-linear "fracture trace" was actually the surface expression of a stratigraphic swale in the Mahoning Coal. Although this discovery provided evidence that photo-linear features are related to geologic structures, this discounted even further the "fracture trace" nature of the feature.

The total range of permeability values determined in these tests is shown in figure 7. (1 foot squared (ft^2) = 929 centimeters squared (cm^2)) These values are averages of each of the step values produced during the multiple-step (abcba) tests. The data appear to be log-normally and possibly bi-modally distributed. This variability is probably the result of several factors, the most important of which is the natural variations of the siltstone's permeability. A secondary factor affecting the data is the impact of mining activity (primarily blasting) on the in situ permeability values of the siltstone. This factor can be given a qualitative analysis by examination of a data subset, the permeability values obtained from Shothole Pattern 5 (Figure 8). The distribution of values for the pattern reveals that permeability increases are highest along the highwall faces of the pattern. The data indicate that increases extend primarily from the recently shot area and that values higher than about 7 x 10^{-13} ft^2 are probably significantly blasting affected. Analysis of other patterns supports these results and indicates that 2x + increases are likely 20 to 30 ft from the shot faces of the tested pattern. This relationship is probably dependent on the thickness of the shot overburden (O'Regan and Nguyen 1981).

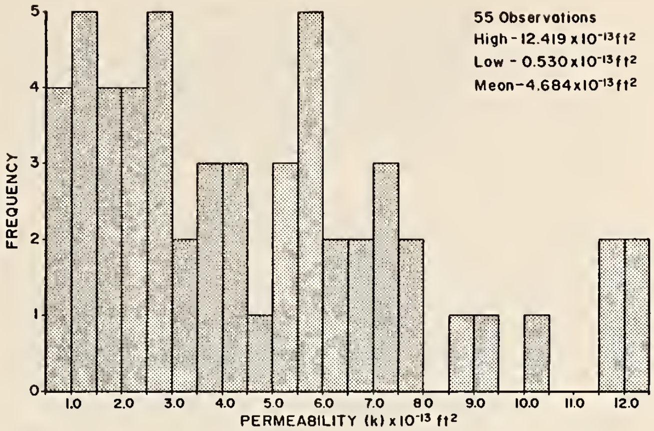

Figure 7 -- Distribution of air-injection permeability values.

The multiple-step nature of the air-injection testing technique made it possible to examine other factors which could influence the permeability data. By preparing test step plots (see examples in figure 9), departures from the ideal linear relationship between flow rate and pressure could be examined (Houlsby 1976). Test 22 had one of the highest permeability values and steepest slopes recorded in this study. Of interest is the fact that the slope of the plot decreases with increasing pressure and flow. This slope change is also

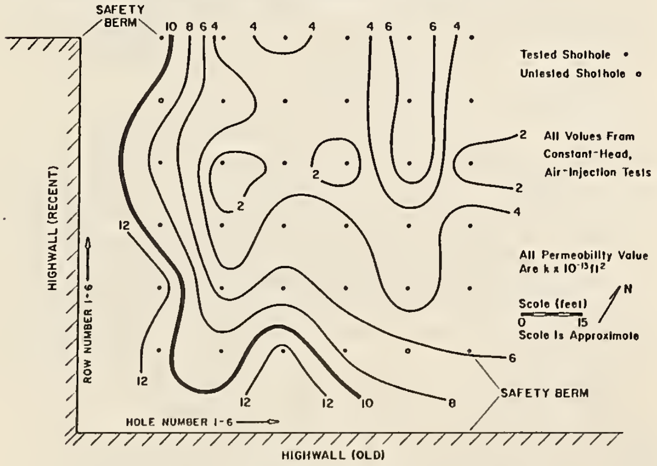

Figure 8 -- Isopermeability map of Shothole Pattern 5.

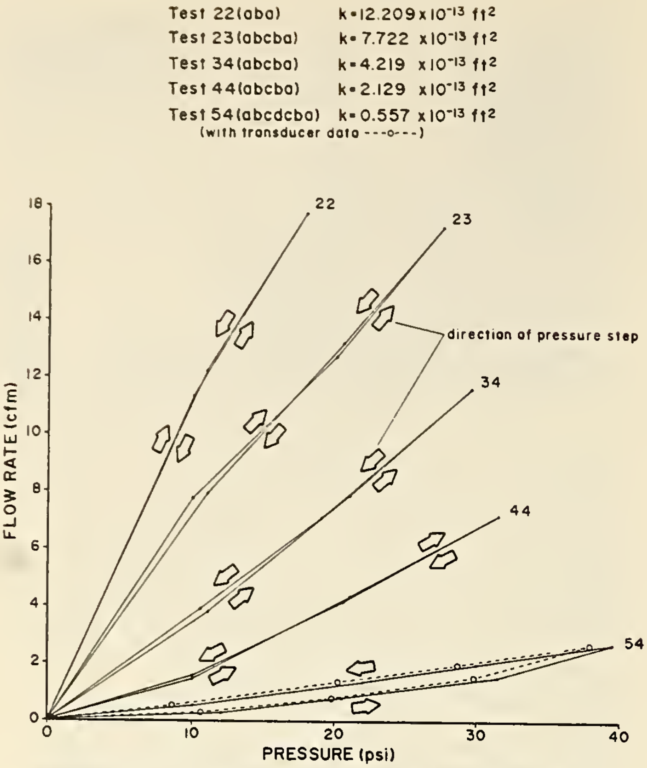

Figure 9 -- Step plots of selected air-injection tests.

illustrated by other high permeability tests, such as Test 23, and it is attributed to either turbulent flow conditions developing in the fractured porous media or to an improved packer seal in the borehole. Test 34, which has a moderate slope and permeability value, illustrates the idealized Darcian relationship between pressure and flow rate. As pressure increases in the test interval, the flow of injected fluid from the test interval increases in an amount which is dependent on the permeability of the material. Test 44 records a slope increase with increasing pressure and flow for a relatively low permeability test. This change is probably the result of the widening of a fracture in the siltstone or the leakage of fluids past the packer unit. Test 54 recorded a very low permeability value and step plot slope. This test was designed to test uphole pressure gauging equipment with downhole transducer readings. The test was conducted in a wet shothole, and the gradual increase in the observed permeability values with increasing pressure and testing time is thought to be due to the displacement of water from pores and fractures which resulted in increasing gas transmission from the test interval. Further analysis to determine the degree of influence of these test factors was not possible with the available testing technique.

Although it should have been possible to apply a Klinkenberg gas slippage correction term to the multiple-step test data, it proved to be impractical due to non-linear variations in the permeability values. The gas slippage correction was developed by Klinkenberg (1941) to account for the increasing interference, and related decrease in observed permeability, between gas molecules as increasing injection pressure makes them behave as an incompressible liquid. In this situation, because the air was not sufficiently compressed to behave as a liquid in these tests, it is possible that the measured permeability values are affected by Klinkenberg slippage.

Other Hydrologic Tests

Because of the restricted number of monitoring boreholes available to be tested by the falling head and constant head water-based tests, as well as field conditions which made some of the holes unsuitable for testing, only two hydraulic conductivity values could be obtained for the siltstone unit. However, the close correlation between these values from Hole 2 (3.9 and 5.1 x 10^{-7} ft/sec for a falling-head and constant-head test respectively) indicates that methods are comparable in this environment. These data and methods may also be comparable to the air-injection technique. This is supported through the use of a data table from Freeze and Cherry (1979) that allows all the air- and water-based test values to be compared. This table (figure 10) shows that the permeability and hydraulic conductivity values are limited in range and appear to represent the equivalent of a permeable sandstone. This does not seem unreasonable because the fractured siltstone unit may be hydrologically similar to such a lithology.

Additional uses of the air-injection technique provided some interesting results. Falling-head air-injection tests

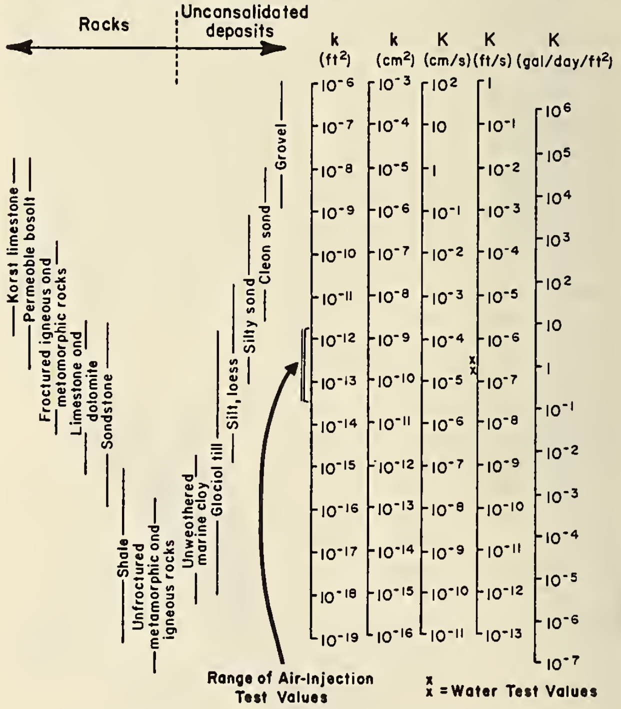

Figure 10 -- Range of test values for permeability (k) and hydraulic conductivity (K) (modified from Freeze and Cherry 1979)

(Blankenship and Stickney 1983) appeared to underestimate permeability values by two orders of magnitude. Air-injection interference testing conducted in Holes 1 and 2 (see figure 1) was more successful. During injection of air through a borehole packer inserted in Hole 2 while monitoring water levels about 20 ft away in Hole 1, it was observed that a water level fluctuation occurred in less than 10 minutes in the monitored hole. This was surprising as it had taken nearly 90 minutes for water injected in Hole 2 (at nearly the same pressure as the air) during the constant-head water-injection test, to cause even a minor change in the water level of Hole 1. The air-injection test also caused a much more substantial change in the observed water levels, nearly 1.7 ft as opposed to a few tenths of a foot. While the significance of these results is unclear, it is clear that injected air is capable of markedly affecting a ground-water flow field under some circumstances.

CONCLUSIONS AND RECOMMENDATIONS

The investigation of fracture features and in situ permeability values conducted at the Browncrest III surface coal mine succeeded in addressing a number of research objectives. The conclusions and recommendations of this work may assist future studies.

Conclusions

1. The photo-linear "fracture trace" orientation peak, between 320 and 330 degrees, compares well to the orientation of local tributary streams and the maxima of other fracture trace studies for this area.

2. The joints mapped in this study had an orientation maxima between 320 and 340 degrees. This agrees well to the fracture trace orientation peak, as well as to the orientation of the local stream valleys and to other published joint data. As a result, it is believed that all the features may be related to a common structural origin.

3. Measurements of joint frequency per highwall traverse interval revealed that joint concentrations appear to be related to specific stratigraphic features rather than fracture traces.

4. The photo-linear feature that was to be the focus of this study was found to be unrelated to a zone of fracture concentration. This feature was found to be related to a stratigraphic swale, possibly an old distributary channel, in the Mahoning Coal.

5. The air-injection technique was found to be quite consistent, durable, and mobile in operation. It was capable of conducting tests for a specific range of conditions: a) boreholes at depths of up to 70 ft, b) hole diameters of 4 to 7 inches, and c) injection pressures and flow rates well in excess of test parameters.

6. The in situ permeability values observed in this study ranged from 0.5 to 12.5 x 10^{-13} ft^2 and appeared to be log-normally and possibly bi-modally distributed. Mining activity was determined to affect the permeability values, increasing values by 2x + up to 30 ft from mine highwalls. As a result, the background permeability of the siltstone unit is probably in the range 1.0 to 7.0 x 10^{-13} ft^2.

7. Factors affecting the air tests were examined through graphical analysis of the test data. Turbulent flow conditions are thought to have the greatest impact on the values, although partially saturated conditions (water in the siltstone) and Klinkenberg slippage may also significantly affect the values.

8. Hydraulic conductivity values obtained by falling-head and constant-head water-based tests from the siltstone unit compare well to the air-based permeability values. These values indicate that the fractured siltstone unit has a character similar to a moderately permeable sandstone.

9. Additional uses and modifications of the air-injection technique were also investigated. Interference testing offers interesting data, although it is not possible to evaluate this information at this time.

Recommendations

Although this study was not able to quantify the subsurface nature of a photo-linear fracture trace, the methods presented here define a means of achieving this objective. However, the reliability, speed, safety, precision, and economics of these techniques may require further investigation. The photo-linear analysis may identify geologic structures, as well as nongeologic ones, that are not related to zones of fracture concentration in the subsurface. The highwall surveys are time consuming, occasionally dangerous, and are complicated by blast fractures and the relationship of the fractures to the highwall orientation. Many factors affect the air-injection technique. However, most of them are inherent to the technique and can only be corrected with improved analysis routines or increasingly costly instrumentation. Therefore, although this technique may be appropriate under circumstances where a high density of data is required, it may not be appropriate for more general investigations (Shuman 1987).

ACKNOWLEDGEMENTS

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MODELING SULFATE RETENTION IN A LAKE RECEIVING ACID MINE DRAINAGE[1]

Alan T. Herlihy, Aaron L. Mills, and Winston Lung[2]

Abstract. -- Bacterial sulfate reduction in the sediments of Lake Anna, VA combined with geochemical processes in the water column remove half the SO_4^{2-} entering the lake in acid mine drainage (AMD) from Contrary Creek. In addition to SO_4^{2-} removal, the pH of the water is increased from about 3.5 to 6.0 within the boundaries of the contaminated arm. A simple water quality model was constructed to predict the spatial and temporal distribution of SO_4^{2-} in the lake water and to help identify the important processes controlling the distribution of the pollution in the lake. The model successfully predicted distribution of SO_4^{2-} in most locations, except for those closest to the mouth of the AMD stream. The model demonstrated that chemical stratification of the lake water was more important than thermal stratification near the mouth of the acid mine stream and that a strong chemical gradient there inhibits vertical mixing. Maintenance of the AMD plume near the sediment surface where the biological activity occurs likely enhances SO_4^{2-} removal. The proportion of SO_4^{2-} retained in the Contrary Creek arm (SO_4^{2-} retained / SO_4^{2-} influx) was 0.48, consistent with other lakes which actively retain sulfur in the sediments. The comparatively short residence time of this arm of Lake Anna (ca. 100 days) yields an SO_4^{2-}-removal coefficient of 12 to 14, which is over an order of magnitude higher than reported for lakes acidified experimentally or by precipitation. In those lakes diffusion is assumed to be the major mechanism of SO_4^{2-} transport to the sediments where most SR occurs. In Lake Anna, the model results demonstrated that some other mechanism plays an important role in transporting the AMD constituents from the lake water to the sediments. The amount of AMD neutralized by the biogeochemical processes in this lake suggests that some impoundments might be appropriate for the renovation of AMD-contaminated waters.

INTRODUCTION

In Lake Anna, VA, successful neutralization of AMD from a series of abandoned pyrite mines occurs within one arm of the lake within 2 km of the point where Contrary Creek enters the lake. Contrary Creek has an annual average pH about equal to 3.2, SO_4^{2-} about equal to 1 to 20 µmol/L, and total iron about equal to 10 to 50 mg/L. On average, 48 % of the SO_4^{2-} that enters the lake from Contrary Creek is removed in the first two kilometers of the lake (Herlihy et al., 1987). Concomitantly, the pH rises to approximately 6 and the iron levels drop to levels similar to uncontaminated arms of the lake. This homeostatic renovation of the water has been attributed to anaerobic bacterial activities, specifically sulfate reduction (SR) in the sediments underlying the contaminated arm of the lake (Mills 1985, Mills and Herlihy 1985, Herlihy and Mills 1985, Herlihy et al. 1987; Mills et al. in press).

The establishment of anaerobic conditions, SR, and the resultant precipitation of metal sulfides are significant in increasing the pH and reducing the AMD-derived iron and SO_4^{2-} concentrations in the lake water. Alkalinity generation from SR occurs according to the equation:

$$2CH_2O + SO_4^{2-} \qquad H_2S + 2HCO_3^{2-}. \quad (1)$$

Evaluation of the relative amount of neutralization that SR can provide is related to the amount of SO_4^{2-} removed from the water. Although SR plus dilution provides a thorough cleansing of water in the Contrary Creek Arm of Lake Anna, prediction of the efficiency of this homeostatic process in other systems must rely on an adequate quantitative model to test other systems prior to construction of new impoundments or contamination of pre-existing waters. The present study applied a modified version of the WASP model (Water Quality Analysis Simulation Program) to simulate the conditions in Lake Anna, with the intent of applying the model to other acidified impoundments in the future.

METHODS

Model Description

WASP is a general model capable of handling one, two, or three dimensional time-variable calculations (DiToro et al. 1983). The water body to be modeled is divided into segments and mass balance equations for each segment are constructed for the constituent of interest. The mass balance equations are solved using a finite difference technique with a backwards-difference approximation in the spatial plane and a forward-difference approximation in the temporal plane. The finite difference equations are integrated using a second-order Runge-Kutta method. WASP has been used successfully in modeling lake acidification in Bickford Reservoir, and Woods and Panther Lakes (Lung, 1987)

Application of WASP to Lake Anna

Only the area of the lake between the mouths of Freshwater and Contrary Creeks and the Route 652 bridge near station A2 was included in the model (fig. 1). To implement WASP in the Contrary Creek arm of Lake Anna, this part of the lake was divided into eight segments (fig. 1). Epilimnion and hypolimnion segments were included for areas of the lake around stations C2, C5, and A2. The Freshwater Creek section of the lake was treated as one segment as was the small segment of lake near the mouth of Contrary Creek around station C1. Sulfate concentration was the only constituent modeled, as SO_4^{2-} retention approximates the neutralization process for the lake.

The flows into each segment of the model are shown diagrammatically in figure 1, and the mass balance and discharge and loading equations are given in table 1. Sulfate from Contrary Creek enters into segment 1, and 90% flows into segment 5 (hypolimnion of station C2) with the remainder flowing into segment 2 (epilimnion of station C2). Water from segment 2 flows into segment 3, and then segment 4 along the surface of the lake (epilimnion segments of stations C5 and A2) before exiting out the outflow. Water in segment 5 flows into segment 6 and then segment 7 along the bottom of the lake (hypolimnion segments of stations C5 and A2) before exiting out the outflow. Sulfate is mixed between the epilimnion and hypolimnion of each station (segments 2 and 5, 3 and 6, and 4 and 7) by vertical eddy diffusion. Flow percentages were calculated from lake cross sectional areas and current velocity observations. Water and SO_4^{2-} from Freshwater Creek enter into segment 8, and then 38% flows into segment 4 and the remaining 62% into segment 7. Each surface segment (1,2,3,4 and 8) received SO_4^{2-} and water from

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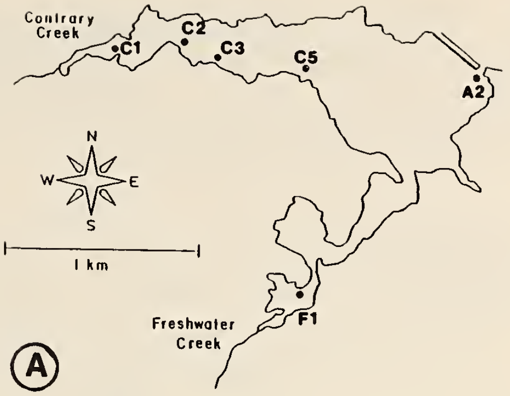
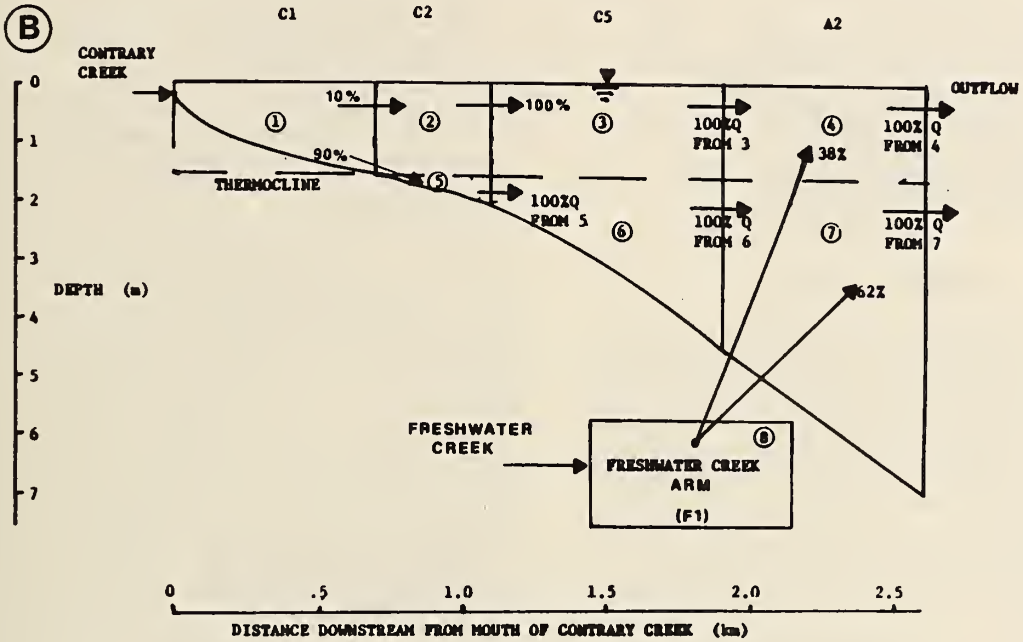
Figure 1. -- **A.** Map of the Contrary Creek arm of Lake Anna. Water flows in an easterly direction. The area shown represents about 13% of the total surface area of the impoundment which lies to the northeast and southeast of the arm shown. **B.** Schematic diagram of flow routing and segment location for the model applied to the Contrary Creek arm of Lake Anna.


Contrary Creek
C1
C2
C3
C5
A2
N
W
E
S
1 km
Freshwater Creek
F1
A


B
C1
C2
C5
A2
CONTRARY CREEK
OUTFLOW
0
1
2
3
4
5
6
7
DEPTH (m)
10%
100%
90%
THERMOCLINE
①
②
③
④
⑤
⑥
⑦
⑧
100%Q FROM 3
100% Q FROM 4
38%
100%Q FROM 5
100% Q FROM 6
100% Q FROM 7
62%
FRESHWATER CREEK
FRESHWATER CREEK ARM (F1)
0
.5
1.0
1.5
2.0
2.5
DISTANCE DOWNSTREAM FROM MOUTH OF CONTRARY CREEK (km)

precipitation and direct input (overland flow and ephemeral streams) and lost water due to evaporation. Sulfate is removed from the segments overlying sediments (1,5,6,7 and 8) by SR minus sulfide oxidation (Herlihy et al. 1987).

The data needed by WASP to run the model (described later) included the volume and initial SO_4^{2-} concentration of each segment, the waterflows between each segment, the eddy diffusion between segments, and the external SO_4^{2-} load into each segment of the model. The kinetic term for SR and the associated coefficients were also input. Finally boundary conditions indicated the sulfate concentration of the outflow from segments 4 and 7.

Flow, Load and Concentration Data

The model was calibrated using data collected during the 1984 water year (October 1, 1983 to September 30, 1984) and verified using data collected during the 1983 water year. Discharges and loads were input into the model at 5-day intervals using the mean value of the five daily discharges and loads. Discharge and load data were taken from the measured sulfate budget for the lake (Herlihy et al. 1987), recalculated for each segment. Initial conditions and boundary conditions were taken from the observed lake water sulfate concentrations. Segment volumes and surface areas were obtained from Bruckner (1986).

Table 1. -- Mass balance and loading and discharge equations used in the application of the modified WASP model to Lake Anna.

MODEL MASS BALANCE EQUATIONS

$V_1 dC_1/dt = W_1 - Q_{12}C_1 - Q_{15}C_1 - k_{sulf}C_1A_1$

$V_2 dC_2/dt = W_2 + Q_{12}C_1 - Q_{23}C_2 + K_zA_{25}/L_{25}(C_5-C_2)$

$V_3 dC_3/dt = W_3 + Q_{23}C_2 - Q_{34}C_3 + K_zA_{36}/L_{36}(C_6-C_3)$

$V_4 dC_4/dt = W_4 + Q_{34}C_3 + Q_{84}C_8 - Q_{40}C_4 + K_zA_{47}/L_{47}(C_7-C_4)$

$V_5 dC_5/dt = Q_{15}C_1 - Q_{56}C_5 + K_zA_{25}/L_{25}(C_2-C_5) - k_{sulf}C_5A_{25}$

$V_6 dC_6/dt = Q_{56}C_5 - Q_{67}C_6 + K_zA_{36}/L_{36}(C_3-C_6) - k_{sulf}C_6A_{36}$

$V_7 dC_7/dt = Q_{67}C_6 + Q_{87}C_8 - Q_{70}C_7 + K_zA_{47}/L_{47}(C_4-C_7) - k_{sulf}C_7A_{47}$

$V_8 dC_8/dt = W_8 - Q_{84}C_8 - Q_{87}C_8 - k_{sulf}C_8A_8$

V_i = Volume of segment i (m^3).
C_i = Concentration of sulfate in segment i (mol/m).
Q_{ij} = discharge from segment i to segment j (m^3/day).
W_i = external sulfate loading into segment i (mol/day).
K_z = vertical eddy diffusion coefficient (m^2/day).
A_{ij} = surface area between segments i and j (m^2).
A_i = surface area of segment i (m^2).
L_{ij} = sum of the depths of segments i and j (m).
k_{sulf} = sulfate removal coefficient (m/day).

$Q_{56} = Q_{15}$

$Q_{67} = Q_{56}$

$Q_{08} = Q_{fc} + S_8Q_{fc} + A_8Q_{prec} - A_8Q_{evap} - A_8Q_{store}$

$Q_{84} = 0.38 * Q_{08}$

$Q_{87} = 0.62 * Q_{08}$

$Q_{40} = Q_{34} + Q_{84} + Q_{04}$

$Q_{70} = Q_{67} + Q_{87}$

Note that segment 0 represents external boundary condition.

Q_{ij} = discharge from segment i to segment j.
Q_{cc} = discharge from Contrary Creek.
Q_{fc} = discharge from Freshwater Creek.
Q_{prec} = water input from precipitation.
Q_{evap} = water loss due to evaporation.
Q_{store} = discharge due to change in lake storage volume.
S_i = ratio of direct input watershed area in segment i to the Freshwater Creek watershed area.
A_i = ratio of lake surface area in segment i to total lake surface area.

DISCHARGE EQUATIONS

$Q_{01} = Q_{cc} + S_1Q_{fc} + A_1Q_{prec} - A_1Q_{evap} - A_1Q_{store}$

$Q_{02} = S_2Q_{fc} + A_2Q_{prec} - A_2Q_{evap} - A_2Q_{store}$

$Q_{03} = S_3Q_{fc} + A_3Q_{prec} - A_3Q_{evap} - A_3Q_{store}$

$Q_{04} = S_4Q_{fc} + A_4Q_{prec} - A_4Q_{evap} - A_4Q_{store}$

$Q_{12} = 0.02 * Q_{01}$

$Q_{23} = Q_{12} + Q_{02}$

$Q_{34} = Q_{23} + Q_{03}$

$Q_{15} = 0.98 * Q_{01}$

LOADING EQUATIONS

$W_1 = W_{cc} + A_1W_{prec} + S_1W_{fc}$

$W_2 = A_2W_{prec} + S_2W_{fc}$

$W_3 = A_3W_{prec} + S_3W_{fc}$

$W_4 = A_4W_{prec} + S_4W_{fc}$

$W_8 = W_{fc} + A_8W_{prec} + S_8W_{fc}$

W_i = external sulfate loading into segment i.
W_{cc} = sulfate loading from Contrary Creek.
W_{fc} = sulfate loading from Freshwater Creek.
W_{prec} = sulfate loading from precipitation.

Vertical Eddy Diffusion Coefficients

Sulfate transport via vertical eddy diffusion was calculated as the product of the vertical diffusion coefficient (K_z) and the interfacial area between the epilimnion and hypolimnion divided by the average depth of the two layers. There are no data about the magnitude of the vertical eddy diffusion coefficient in Lake Anna, so a value of 0.05 cm^2/sec was chosen as a first approximation of K_z, based on a range of literature values for a number of similar and dissimilar lakes.

Sulfate Removal Kinetics

Sulfate removal was modeled by the equation

$$V_i * dC_i/dt = k_{sulf} * C_i * A_i \qquad (2)$$

where C_i is the SO_4^{2-} concentration in segment i (mols/m^3), A_i is the surface area of segment i (m^2), V_i is the volume of segment i (m^3) and k_{sulf} is the sulfate removal coefficient (m/yr). Sulfate removal only takes place in segments overlying sediments. As modeled here, k_{sulf} describes the net reaction of sulfate reduction minus sulfide oxidation. The coefficient can be thought of as a piston velocity relating how many meters of water per year must be processed by the sediments to account for the observed sulfate removal.

Baker et al. (1986) presented an equation for calculating k_{sulf} based on the mean depth, water residence time, and sulfate retention of a lake:

$$k_{sulf} = R * z / (t_w * (100-R)). \qquad (3)$$

In this equation, R is the retention of SO_4^{2-} as percentage of input, t_w is the water residence time (yr.), and z is the mean depth (m). Values of k_{sulf} in the present study were then calculated using the budget data from Herlihy et al. (1987). The average depth was calculated by dividing the Contrary Creek arm lake volume by its surface area (4.4×10^6 m^3 / 1.1×10^6 m^2 = 4 m). Calculated values of k_{sulf} were 12.7 m/year in the 1983 water year and 14.1 m/year for the 1984 water year. These coefficients were used in the model in the kinetic expression for sulfate removal as shown in equation 2.

RESULTS

Model Calibration

Average epilimnetic and hypolimnetic sulfate concentrations predicted by the model for the 1984 water year were in good agreement with observed data. However, the model predicted little chemical stratification between epilimnion and hypolimnion using a K_z of 0.05 cm^2/sec. The observed SO_4^{2-} data showed a strong stratification at station C2 during most of the year and at station A2 in the winter. Therefore the model was rerun after changing the spatial and temporal values of K_z so that a reasonable fit to the data set was obtained. The K_z values for stations C5 and A2 were lowered to 0.01 cm^2/sec. In order to obtain a good fit to the observed station C2 data, the K_{z2} had to be lowered even more to 0.002 cm^2/sec. It was also necessary to change the flow routing so that 98% of the water from Contrary Creek coming from segment 1 went into segment 5 (C2 hypolimnion). In order to fit the observed winter sulfate distribution at station A2, it was necessary to decrease all three K_zs to 1×10^{-5} cm^2/sec from December 25 to February 15 to reflect the reduction in vertical diffusion due to ice cover on the lake. The ice cover would lower K_z by stopping any wind mixing.

To make the model more realistic, k_{sulf} was set to 0 during the months of January and February to reflect the cessation of sulfate removal as observed previously (Herlihy, 1987). During October, November, and December, k_{sulf} was decreased linearly with time from the maximum summer value to zero. Similarly during March, April, and May, k_{sulf} was increased linearly with time from zero to the maximum summer value. The maximum summer k_{sulf} (in effect from June through September) was calculated so that the value calculated in equation 3 was the annual average k_{sulf}.

After these calculations, the predicted SO_4^{2-} concentrations in both epilimnion and hypolimnion at station C2 were in fairly good agreement with the observed data (fig. 2). The model failed to predict the low hypolimnetic SO_4^{2-} concentrations in June and July. The model also underestimated SO_4^{2-} concentration in the epilimnion from October to April and overestimated it from July to September.

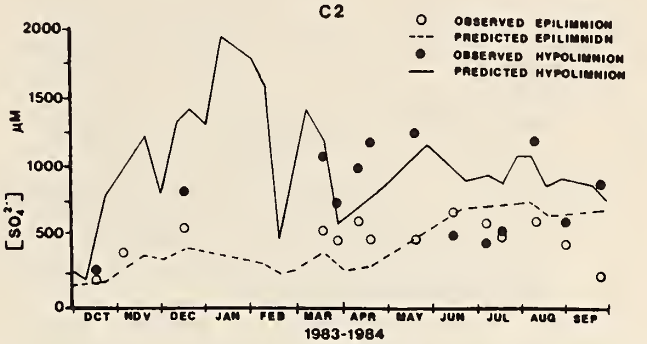


Figure 2. -- Observed and model-predicted sulfate concentrations (µmol/L) in the epilimnion and hypolimnion at station C2 (segments 2 and 5) during the 1984 water year.

The model predicted SO_4^{2-} concentrations at station C5 (fig. 3) better than it did at station C2. Most of the observed SO_4^{2-} concentrations were within 10-20% of the predicted concentrations. At station A2 the model predicted the observed SO_4^{2-} stratification in January and February (fig. 4). From June through September, the predicted SO_4^{2-} concentrations in the hypolimnion were about 50% lower than the observed concentrations.

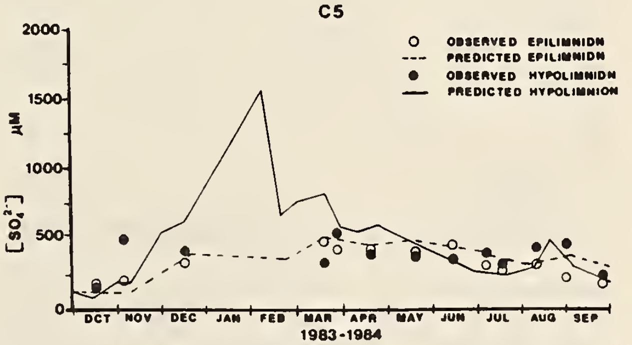


Figure 3. -- Observed and model-predicted sulfate concentrations (µmol/L) in the epilimnion and hypolimnion at station C5 (segments 3 and 6) during the 1984 water year.

Sensitivity Analysis

To understand the sensitivity of the model to k_{sulf} and K_z a sensitivity analysis of these parameters was

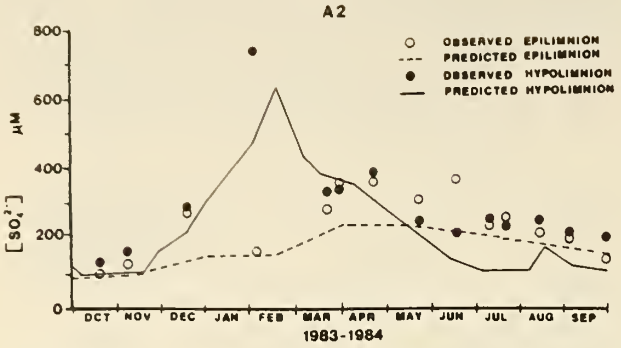


Figure 4. -- Observed and model-predicted sulfate concentrations (µmol/L) in the epilimnion and hypolimnion at station A2 (segments 4 and 7) during the 1984 water year.

performed. The predicted sulfate concentration in the hypolimnion at station A2 was very sensitive to small changes in k_{sulf} (fig. 5). The solid line in the middle of figure 5 was the 1984 value of k_{sulf} calculated from equation 3 (14.1 m/yr). The line predicting higher SO_4^{2-} concentrations represents an annual k_{sulf} of 1.85 m/yr and the lower SO_4^{2-} concentration line had a value of 70.0 m/yr. All of the k_{sulf} values in this exercise were set to 0 during the winter months and varied with time as described above. The sensitivity analysis shows that the range of acceptable values of k_{sulf} is small, about 5-20 m/yr.

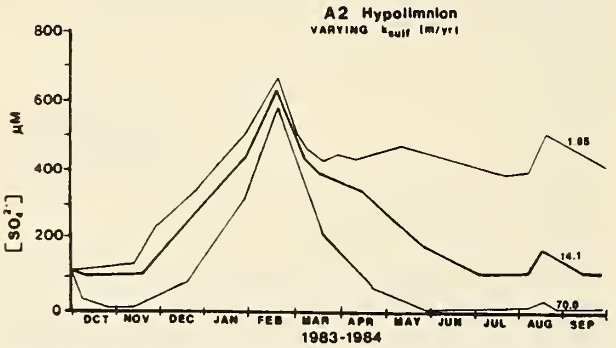


Figure 5. -- Model-predicted sulfate concentrations in the hypolimnion of station A2 (segment 7) at varying values (m/ yr) of the sulfate removal coefficient (k_{sulf}).

The sensitivity analysis for K_z showed that large (order of magnitude) changes made small, but significant changes in the predicted epilimnetic SO_4^{2-} concentration at station C2 (fig. 6). With a K_z of 1 x 10^{-4} cm^2/sec there was little or no mixing between epilimnion and hypolimnion. Thus, predicted SO_4^{2-} concentrations were low and remained fairly constant with time

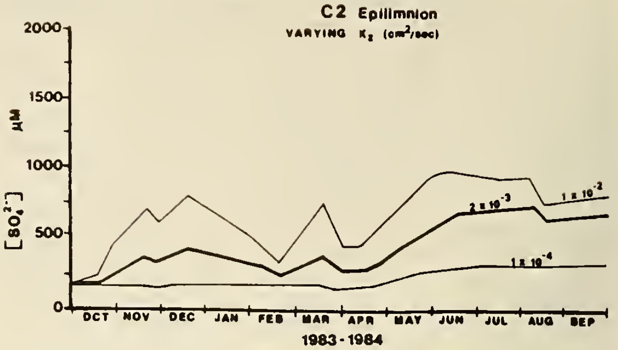


Figure 6. -- Model-predicted sulfate concentrations (µmol/L) in the epilimnion of station C2 (segment 2) at varying values (cm^2/ sec) of the vertical eddy diffusion coefficient (K_z).

because waterflow through the epilimnion was low (only 2% of Contrary Creek inflow), and there was little SO_4^{2-} influx from direct input and precipitation. There was more SO_4^{2-} transfer between hypolimnion and epilimnion when K_z was 1 x 10^{-2} cm^2/sec. The effects of different K_z values on the predicted hypolimnetic SO_4^{2-} concentrations at station C2 were less than 10% (data not shown).

Model Verification

The model was verified using data collected during the 1983 water year and the same values of K_z used in the calibration. The value of k_{sulf} used in the verification was 12.7 m/yr, and it was varied temporally as described above. The predicted SO_4^{2-} concentrations in the hypolimnion at station C2 were higher than the observed concentrations but the trends were similar (fig. 7). Observed epilimnetic SO_4^{2-} concentrations were scattered around the predicted concentration line.

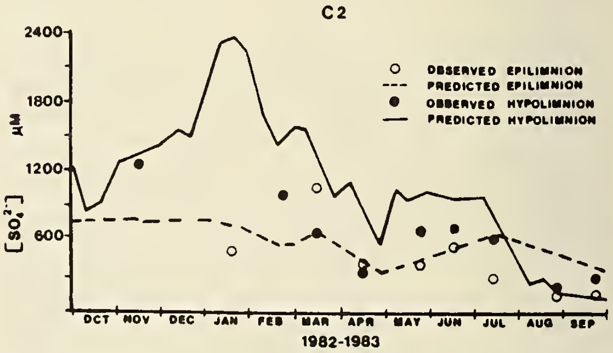


Figure 7. -- Observed and model-predicted sulfate concentrations (µmol/L) in the epilimnion and hypolimnion at station C2 (segments 2 and 5) during the 1983 water year.

Except for the late winter and early spring months, the observed and predicted SO_4^{2-} concentrations at station C5 were in good agreement (fig. 8). The high SO_4^{2-} concentrations predicted in the hypolimnion in the winter were not seen in the observed February and March data. The predicted and observed SO_4^{2-} concentrations at station A2 were also similar except for the predicted hypolimnetic sulfate peak in February and March that was not present in the observed data (fig. 9). Model efficiency was calculated using the verification data (predicted and observed) from March through September 1983. F values (sum of the squares of the observed data about the mean divided by the sum of the squares of the predicted data-observed data) were very low (ranging from 0.19 in the A2 hypolimnion to 2.03 in the A2 epilimnion); there was as much variance in the model prediction about the observed data as in the observed data about the mean.

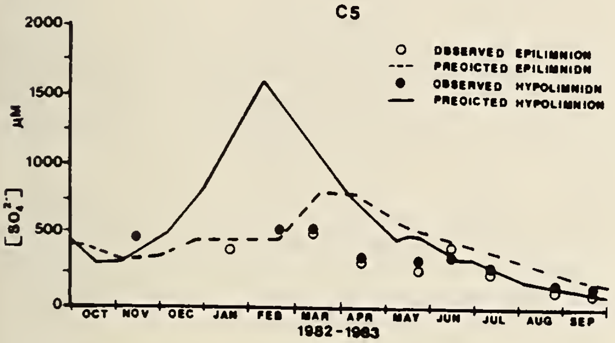


Figure 8. -- Observed and model-predicted sulfate concentrations (µmol/L) in the epilimnion and hypolimnion at station C5 (segments 3 and 6) during the 1983 water year.

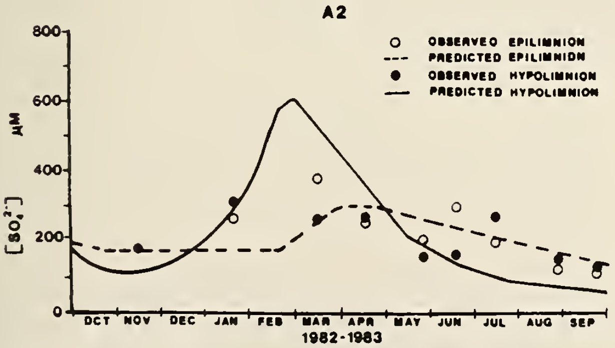


Figure 9. -- Observed and model-predicted sulfate concentrations (µmol/L) in the epilimnion and hypolimnion at station A2 (segments 4 and 7) during the 1983 water year.

DISCUSSION

In order to fit the model to the observed data, it was necessary to assume that 98% of the AMD inflow went into the hypolimnion of C2 and that K_z at station C2 was lower than the other stations. At C2 the more AMD impacted water in the hypolimnion has a higher density than the epilimnetic water so there is a barrier to mixing that would cause a lower K_z. At stations C5 and A2 the chemical gradient has been reduced by SO_4^{2-} and metal removal, dilution, and mixing so that the chemical barrier to mixing is reduced and a higher K_z would be expected. At certain times in the year, especially at station C2, the observed and predicted SO_4^{2-} concentrations were not very close. It is likely that the actual K_z varies more temporally than the K_z used in the model. Factors such as storm events, and large changes in air temperature, and wind direction could cause large changes in K_z for short periods of time. A storm event would carry in a large amount of dilute water destroying a chemical stratification and perhaps causing turbulent mixing. Similarly, the SO_4^{2-} maximum predicted by the model in January and February 1983 was not seen in the observed data. The ice cover in 1983 was much less than it was in 1984. If ice cover was the factor reducing K_z in the winter of 1984, it is likely that the K_z in the winter of 1983 should not have been as low as it was modeled. Actual measurements of K_z with time and the percent of AMD inflow entering the hypolimnion would enhance the predictive ability of the model.

Baker et al. (1986) reported a mean k_{sulf} of 0.46 (± 0.30) m/yr for 14 softwater lakes. They found that k_{sulf} was inversely related to the lake's residence time. Lakes with a long residence time allow more time for SR to remove SO_4^{2-} yielding a higher SO_4^{2-} retention. Lakes with a short residence time, like Lake Anna, had a low SO_4^{2-} retention (<10% of input) since the SO_4^{2-} is rapidly flushed out of the lake. The values of k_{sulf} in Lake Anna (12-14 m/yr) were almost two orders of magnitude greater than the values reported by Baker et al. (1986). The implications of this drastic difference could be attributed to different SO_4^{2-} removal mechanisms. The lakes sampled by Baker et al. were all affected by acid precipitation, not AMD, and diffusion was said to be the major mechanism for SO_4^{2-} transport into the sediments. In Lake Anna, diffusion could account for no more than 5% of the observed SO_4^{2-} removal from the lake (Herlihy et al. 1987). A mechanism with a more rapid SO_4^{2-} transport rate could account for the higher k_{sulf} observed in Lake Anna. It has been hypothesized that SO_4^{2-} is transported to the sediment via adsorption onto settling solid particles or iron floc (Mills et al. in press).

Therefore the higher iron concentrations in Lake Anna could account for the higher k_{sulf}. The value of k_{sulf} in Lake Anna needed to make the model results match the observed results supports the hypothesis that some mechanism operating much more rapidly than diffusion is working to transport SO_4^{2-} to the sediments.

Another possible improvement to the model would be to adjust the SO_4^{2-} removal coefficient to account for the iron concentration. If iron flocculation is the major SO_4^{2-} transport mechanism then it is important to account for this process in the model. It is likely that SO_4^{2-} removal is most rapid near the mouth of Contrary Creek where the majority of the iron precipitates.

CONCLUSIONS

In order to accurately model the observed sulfate distribution in Lake Anna it was necessary to reduce both the vertical diffusion coefficient and the amount of Contrary Creek water flowing into the epilimnion. The steep chemical gradient near the mouth of Contrary Creek effectively inhibits vertical mixing. The observed data showed a great deal of fluctuation at station C2 indicating that the actual pattern of creek inflow and vertical diffusion has a great deal of temporal variability.

The predicted SO_4^{2-} concentration in Lake Anna was very sensitive to the SO_4^{2-} removal coefficient. The model results showed that the SO_4^{2-} removal coefficient could be calculated successfully using equation 3. The removal coefficient in Lake Anna was more than an order of magnitude higher than observed in lakes where diffusion is the major mechanism of SO_4^{2-} transport to the sediments. Thus some other transport mechanism plays an important role in removing SO_4^{2-} from Lake Anna.

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PENNSYLVANIA'S APPROACH TO CUMULATIVE HYDROLOGIC IMPACT ASSESSMENT OF COAL MINING ACTIVITIES[1]

Lynn E. Langer[2]

Abstract.--Pennsylvania's regulations require that an assessment be made of probable cumulative hydrologic impacts of all anticipated coal mining in the general area of a proposed mining operation and that the proposed operation be designed to prevent damage to the hydrologic balance. The cumulative hydrologic impact assessment (CHIA) process, therefore, consists of two steps: (1) definition of potential damage to the hydrologic balance, and (2) prevention of such damage. Damage to the hydrologic balance is referenced to quality, quantity, and present uses of surface and ground water systems. The Pennsylvania Department of Environmental Resources' (DER's) approach is to describe existing hydrologic conditions and potential adverse effects from mining in two-phase reports on watersheds of 20 to 50 mi^2. The Phase I CHIA Report is a brief description of the watershed and a synopsis of surface and ground water uses and present and potential impacts from mining. The Phase II CHIA Report is a more detailed discussion of geology, hydrology, and mining history in the watershed. DER has found that insufficient data exist to adequately define existing hydrologic conditions. The phase approach allows available core information to be disseminated on a large number of watersheds while hydrologic data collection for more detailed assessment progresses. Prevention of damage to the hydrologic balance is accomplished primarily through evaluation of individual proposed mine sites. Because Pennsylvania's cumulative impact assessment program is based on existing permit review mechanisms, a permit reviewer can perform a mine site assessment even when a Phase I or II CHIA for the appropriate watershed has not yet been written. The major challenge which Pennsylvania faces in implementing its CHIA program is in assuring the equitableness of effluent restrictions within individual watersheds.

INTRODUCTION

In order to obtain primacy in regulating its coal mining industry, Pennsylvania was required to make numerous changes in its existing regulations. One change was the addition of a requirement that the regulatory agency (in this case, the Pennsylvania Department of Environmental Resources) evaluate each mining permit application in light of all existing and proposed mining operations in the general area and make an assessment of the probable cumulative hydrologic impacts. Proposed mining activities must be designed to prevent damage to the hydrologic balance within and outside the proposed permit area (25 Pa. Code Section 86.37(a)(4), which is based on 30 CFR Section 773.15(c)(5)). This Pennsylvania regulation went into effect in 1982.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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The cumulative hydrologic impact assessment, or CHIA, process consists of two steps: (1) definition of damage to the hydrologic balance, and (2) prevention of such damage. Under Pennsylvania regulations, damage to the hydrologic balance is referenced to quality and quantity of surface and ground water systems and to the present uses of the surface and ground water. Because these conditions vary from area to area, the definition of damage to the hydrologic balance does also. Accordingly, the first step of the CHIA process is to delineate the cumulative impact area and describe the current physical and hydrologic conditions of that area. Existing and proposed surface and ground water uses are defined, and the susceptibility of those uses to potential adverse effects from mining activities is evaluated. Prevention of damage to the hydrologic balance (the second step of the CHIA process) involves a prediction of potential impacts from mining activities and efforts needed to prevent adverse impacts.

In developing a CHIA program, DER has expanded on its own existing mechanisms for accomplishing both steps of the cumulative hydrologic impact assessment process. The CHIA has become a set of written documents wherein damage to the hydrologic balance is defined primarily in two-phase reports on watershed areas and efforts to prevent hydrologic damage are addressed primarily in written assessments for individual mine sites.

BACKGROUND

Pennsylvania's environmental regulations require cumulative hydrologic impact analyses for six types of mining activities: surface and underground mining of bituminous coal, surface and underground mining of anthracite coal, disposal of coal refuse, and operation of coal preparation plants. The Pennsylvania Department of Environmental Resources (DER) is the regulatory agency responsible for reviewing permit applications and, consequently, for making impact analyses. Because DER receives more permit applications for bituminous surface mines than for other types of coal activities, the agency has been orienting its initial efforts in development and implementation of the CHIA program toward bituminous surface mining, which will be the main thrust of this paper.

Although Pennsylvania's formal program for cumulative hydrologic impact analysis is in the first stages of implementation, elements of CHIA have existed in the permit review program for a number of years. These elements include: (1) statewide designation of "Special Protection" watersheds, where waste discharges of any nature are restricted; (2) mining management plans for sensitive watersheds; and (3) review of each proposed mine site for hydrologic interactions with adjacent mines.

Pennsylvania designates streams having excellent quality water and high public resource value as Special Protection streams, specifically "Exceptional Value Waters" and "High Quality Waters". Regulations prohibit degradation of ambient stream water quality in Exceptional Value Waters, which virtually eliminates further mining in those watersheds. High Quality Waters may be degraded from ambient quality if the discharge is a result of a project having public value and if downstream water uses will be protected. Mining operations proposed for High Quality watersheds have been required to meet more stringent permit requirements and have often been restricted in extent and nature. For several years, DER has required discharges from mining operations on High Quality watersheds to meet volume restrictions as well as effluent quality standards in order to provide additional protection to the instream water quality.

In the early 1980's, DER developed mining management plans for watersheds where adverse cumulative impacts from mining were identified. Most of these watersheds were public water supply sources. Typically, the mining management plans required stricter erosion and sedimentation control measures, a limit on disturbed acreage on each mine site, mandatory overburden analysis, and prohibition from mining coal seams which were known to produce acid mine drainage in the watershed. Many of these management plans are still being implemented.

CHIA elements have long been part of the individual mining permit review process. Permit reviewers consider the interaction of the proposed mining activities with adjacent active and abandoned mine sites. Typical analyses done by reviewers include determining probable impacts on the quality and quantity of discharges from underlying underground mines, impacts on surface flow and ground water recharge on adjacent surface mines, and cumulative impacts of several sites on ground water recharge to private water supplies or to wetlands. In recent years, DER has used effluent volume restrictions to address cumulative impacts on stream quality in some non-High Quality watersheds.

The formalized CHIA process incorporates and expands on the existing permit review elements. A standard format for impact analysis was developed to improve consistency of permit review among the various District Offices and help ensure that no aspect of cumulative impact assessment is overlooked. The resulting written format for analysis of impact assessments will also facilitate oversight by the federal Office of Surface Mining Reclamation and Enforcement. Formalization of the CHIA process has ensured a systematic examination of hydrologic impacts by watershed and has revealed a need for an expanded hydrologic data base.

CHIA REPORT ELEMENTS

Phase I CHIA Report

Phase I provides a brief introduction to a cumulative impact area, highlighting areas of concern. For this part of the CHIA process, DER has chosen to use watersheds of 20 to 50 mi^2 as cumulative impact areas. Each Phase I report is a short description of a watershed and a synopsis of surface and ground water uses, coal seams being mined, and previous and potential hydrologic impacts of mining. For permit reviewers, it can increase familiarity with the area and encourage a watershed-scale perspective. It alerts coal operators and consultants to potential impacts they might be expected to address in mine permit applications.

Phase I includes the following subtopics: (1) Hydrologic Unit, (2) Drainage Characteristics, (3) Physiography/Topography, and (4) Special Considerations. The Hydrologic Unit section defines the limits and location of the watershed and delineates it on a map. Drainage Characteristics include basin and subbasin drainage areas, maximum relief, stream lengths, and stream classifications. Physiography/Topography is a brief, general discussion of the physical characteristics of the watershed. These three sections set the stage for the core of the Phase I report, Special Considerations.

Special Considerations include a wide variety of hydrologic concerns. The presence of a public water supply in the watershed is often a major concern. Phase I describes the supply's location, source, and service area and any previous mining-related problems. Private water supplies (usually wells or springs) are common in the rural areas where bituminous surface mining takes place. Because their specific locations and sources are identified in permit applications, little emphasis is placed on reiterating this information in Phase I. Phase I does, however, note any previous adverse impacts on private water supplies in the area, such as diminution or degradation.

As part of the Special Considerations, Phase I identifies water-based recreational uses which could be adversely affected by mining in the watershed. The most common instance is trout fishing in streams stocked by the Pennsylvania Fish Commission. The use of wetlands, streams, and lakes by threatened or endangered species is also noted in this section.

A brief summary of mining history and resultant hydrologic impacts in the cumulative impact area completes the Phase I report. This section identifies the coal seams which have been mined in the watershed and whether they have produced acid mine drainage. A summary of the presence of toxic strata, calcareous strata, channel sandstones, and other strata of interest is made from overburden analyses performed in the area. Existing mining management plans are outlined. The report identifies previous impacts which mining has had on watershed resources and potential future hydrologic impacts from mining.

The Phase I CHIA is based on information from a number of sources. Reports by State and Federal agencies on regional coal hydrology and water resources are helpful for a broad overview, but they generally deal with much larger basin areas than the CHIA reports. For information which is more specific to the cumulative impact area, interviews with mining permit review and inspection staff personnel and review of DER data bases, biological stream surveys, and water quality reports for abandoned mine reclamation projects are useful.

Phase II CHIA Report

In addition to describing vegetation, land uses, and soil types in the cumulative impact area, Phase II discusses watershed geology, hydrology, and mining history in much more detail than Phase I.

Pennsylvania's initial attempt to write a Phase II CHIA revealed that existing water quality and quantity data at key stream points are insufficient to adequately define watershed hydrology. Most existing data fall into two categories: (1) data from stream points with drainage areas larger than CHIA units (such as Pennsylvania Water Quality Network stations or USGS gauge stations); or (2) data from coal operators' water monitoring reports, which include stream points located immediately upstream and downstream of mine sites, but not necessarily at the receiving stream's mouth. In the 20 to 50 mi^2 watersheds which make up Pennsylvania's CHIA units, water quality and quantity data from major tributary confluences and critical points along the main stem (often including the main stem mouth) are minimal or absent.

DER is currently using two approaches to develop the needed data on watershed hydrology -- data collection by DER personnel and data collection by the United States Geological Survey (USGS). Bureau of Mining and Reclamation staff members are collecting quarterly water quality and quantity data from key points (main stem mouth, major tributary confluences, and other points) in two watersheds. Limited staff time prevents the use of this approach for additional watersheds. Therefore, DER is planning to initiate a joint project with the USGS to collect hydrologic data from additional watersheds. The project will be patterned after data collection by USGS on three prototype watershed projects in Pennsylvania which are being funded by the Office of Surface Mining Reclamation and Enforcement. Data collection on these projects includes (1) continuous monitoring of the main stem mouth for stream discharge, pH, specific conductance, and temperature; (2) monthly water quality sampling of the main stem mouth for additional parameters; and (3) four sets of water quality samples and flow measurements from key watershed points taken during baseflow and high flow periods.

DER is also taking steps to increase the amount and availability of site-specific hydrologic data. Since November 1986 the Department has required surface mine operators to measure, rather than estimate, the flows of all stream and discharge points they monitor, thus increasing the amount of reliable water quantity data available. In addition, the Department has completed compilation of existing quality and quantity data on acid mine drainage discharges from surface mines and is entering the results into a computer data base. This data base, categorized by drainage basin, will provide information on the severity and hydrologic impact of each mine drainage discharge, identification of the coal seams mined on the associated site, and a mechanism for prioritization of watersheds for further evaluation.

The hydrology, mining history, and geology sections are expected to be the most useful for permit reviewers and others interested in the CHIA. These sections will serve to document current "baseline" watershed conditions for comparison with future conditions, detail the impacts previous mining has had on the hydrologic balance, and relate those conditions and impacts to the geology of the area. The vegetation, land use, and soils sections will increase in importance if DER finds computer modeling of impacts to be valuable and practical.

If current mining management practices are found to be inadequate to prevent cumulative damage to the hydrologic balance, the Phase II report will also develop recommendations for future management strategies.

Mine Site Assessment

The Mine Site Assessment is a written appraisal of the probable impacts of a specific site on the hydrologic balance, in conjunction with existing and anticipated mine sites in the general area. The Mine Site Assessment describes the proposed mining activities and how they have been planned to prevent damage to the hydrologic balance.

In evaluating potential damage to existing uses of surface and ground water, the permit reviewer relies on hydrologic data and resource information from several sources, primarily the permit application and the Phase I and II CHIA Reports. Because of the information available in the permit application, the inspector's field review report, and reports submitted by other agencies, a permit reviewer can perform a Mine Site Assessment even if the Phase I and II CHIA Reports for that watershed have not yet been written.

Potential cumulative hydrologic impacts are as varied as the hydrologic conditions on potential mine sites. One factor common to all sites, however, is the potential for impact on the quality of the receiving stream immediately downstream of the site.

Under Pennsylvania's environmental regulations, every stream in the state is protected for certain minimum uses (potable water supply, fishing, esthetics, etc.) and also for specific additional uses, according to its classification. Therefore, even though a stream is not currently being used for a specific purpose (like those identified in the Phase I CHIA Report), instream water quality may not be degraded beyond certain criteria. As previously discussed, the Department has been using discharge volume restrictions as a tool for preventing violations of the instream criteria in High Quality watersheds and has been expanding their use to non-High Quality watersheds.

At present, the volume restriction calculations are based on the acreage disturbed by the mine site and the total drainage area upstream of the discharge point. The incorporation of factors such as slope, soils, and vegetation through computer modeling is being explored by DER in a joint project with the U.S. Geological Survey. Implementation of computer modeling in the CHIA program will be dependent on the amount of data collection required for accurate calibration of the model and on the transferability of the calibrated model from one watershed to another.

CHALLENGES IN IMPLEMENTATION

The major challenge which Pennsylvania faces in implementing its CHIA program is in the area of assigning effluent quality and quantity limits. DER strives to be equitable in the restrictions it places on operations within a single watershed. Three approaches exist to accomplish this: (1) base effluent limits on the maximum acreage predicted to be disturbed in the watershed at one time; (2) impose new, stricter limits on existing operations when additional discharges are approved; or (3) establish an upper limit of disturbed acreage for each watershed, and require new operations to wait until older ones are completed.

For the first approach, it is virtually impossible to predict the maximum acreage which will be disturbed at one time in any given watershed. An estimate of remaining mineable coal reserves could be substituted, representing the absolute maximum possible, but this tactic would require significant amounts of information not readily available to the Department. In addition, it could result in measures overly restrictive for protection of the water resources.

The second approach, imposing more restrictive effluent limits on existing operations, may require substantial physical modifications on those sites which might not be technologically or economically feasible.

The third approach, establishing a ceiling on the amount of disturbed acreage, involves considerable administrative effort and may impose economic hardships and planning difficulties on individual mine operators.

CONCLUSIONS

The Pennsylvania Department of Environmental Resources has attempted to develop a practical approach to cumulative hydrologic impact assessment. Existing information on surface and ground water uses and on past and potential hydrologic impacts from mining is made readily available to permit reviewers through Phase I CHIA Reports. Additional key water quality and quantity data are being collected and will be made available, along with detailed geology and mining history discussions, in the Phase II CHIA Reports. The two-phase report allows basic, core information to be disseminated on a large number of watersheds, facilitating permit review, while more detailed data collection progresses. Reviewers of mine permit applications use all available information to make assessments of cumulative hydrologic impacts and to ensure that individual mining operations are designed to prevent damage to the hydrologic balance.

BIOLOGICAL METAL REMOVAL FROM MINE DRAINAGE

Katsutaka Nakamura[1]

Abstract.--Mine drainage contaminated with heavy metals requires proper treatment to avoid pollution of surface waters. The aim of this work was to improve on known biological methods and to develop an economic, cost-effective pilot plant-scale process for removal of metal in mine drainage. Good results were obtained with a continuous-flow fluidized bed-type anaerobic reactor, with a working volume of 180L, in a continuous flow system using Desulfovibrio vulgaris as the principal sulfate-reducing bacteria.

INTRODUCTION

There are a number of inactive and abandoned underground mines in Japan from which acid drainage with heavy metals flows out continuously. To alleviate the acidic condition and metal content in the drainage, the following chemical treatment has been carried out: neutralization by slaked lime and powdered limestone. This chemical treatment, however, is not economically attractive because of its high cost and the occurrence of a large quantity of waste sludge. Therefore, alternative methods are needed.

Since dissolved metals can be removed as sulfide precipitates by anaerobic sulfate-reducing bacteria, various attempts have been made to treat acid mine drainage by this biological methods (Wakao, et al. 1979, Maree and Strydom 1985, 1987).

In this work basic experiments were carried out using Desulfovibrio vulgaris in both laboratory and pilot-scale tests in a continuous flow system. In developing the process, the following aspects were investigated:

(1) Optimum conditions of a process to maintain the biological and chemical reactions: amount of organic carbon, pH level, inflow of raw water, and temperature for reactions
(2) Type of reactor required for effective separation of sulfide precipitate
(3) Continuous process to remove metal from raw water.

LABORATORY-SCALE EXPERIMENT

A strain of Desulfovibrio vulgaris was placed in culture medium shown in table 1 and incubated at 30°C. After incubation for six days, the bacteria grew and the medium turned black in color. The degree of reduction of sulfate to sulfide is shown in figure 1. This enriched culture was used as an inoculum of the culture of sulfate-reducing bacteria used in this experiment.

The experiment was performed in a continuous-flow fluidized bed-type anaerobic reactor with a working volume of 10L. The water used as feed was synthetic, composed of the same elements as shown in table 1. The water was fed continuously to the reactor after sufficient growth of the bacteria. Hydrogen sulfide was bubbled into the solution for mixing and coagulant, polyacrylamide, was added in the reactor to step up precipitation during the run.

Both the Fe^{2+} and Zn^{2+} ion contents in the feed water were set at 50mg/L respectively. Quantity of these metal ions and the sulfate concentration value in the effluent was used as the indicator of the reactions.

The experiment was performed changing

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Table 1.--Chemical characteristics of the culture medium used in the incubation of bacteria and laboratory-scale experiment.

Component	Value
K_2HPO_4	0.5g
NH_4Cl	1 g
Na_2SO_4	1 g
$MgSO_4 \cdot 7H_2O$	2 g
Na-lactate	3.5g
Yeast extract	1 g
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	0.5g
$Cu^{2+}[CuSO_4 \cdot 5H_2O]$	3 g
$Pb^{2+}[Pb(NO_3)_2]$	10 mg
$Zn^{2+}[ZnSO_4 \cdot 7H_2O]$	50 mg
$Cd^{2+}[CdSO_4 \cdot nH_2O]$	1 mg
$As^{3+}[NaAsO_2]$	1 mg
Tap water	1,000 mL
pH	6.0-6.5

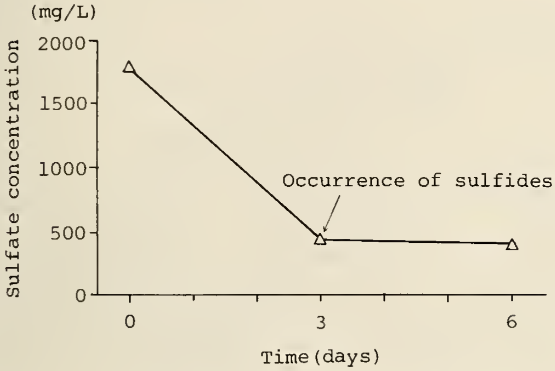

Figure 1.--Degree of decrease of sulfate by sulfate-reducing bacteria, Desulfovibrio vulgaris.

inflow stepwise at 10, 20, 40, and 80L/day, with the pH level between 5.0 and 6.5 and temperature in the reactor at 15°C and 30°C.

Sodium lactate used as the organic carbon source was added first at 3.5g/L and reduced to 1g/L. Yeast extract was started at 1g/L, then cut to zero finally.

Most of the metals in the feed water were separated as sulfides consistently during the periods of continuous operation: metal content in the effluent was kept below the emission standard in Japan ($Fe < 10$ mg/L, $Zn < 5$mg/L, $Cu < 3$mg/L, $Pb < 1$mg/L, $Cd < 0.1$mg/L, $As < 0.5$mg/L).

Concentration of the bacteria in the reactor was measured by the Thoma-Zeiss counting chamber once a week.

The results of the experiment was shown in table 2 and was summarized as follows.

(1) Sodium lactate can be cut down to 1g/L at 20°C and pH5, and to 2g/L at 10°C and pH6

(2) Retention time was 3 hours(80L/day inflow) at 15°C, pH6, sodium lactate 3.5g/L and yeast extract 1g/L, and 6 hours(40L/day inflow) at pH5

Table 2.--Result of the laboratory-scale experiment.

Inflow (L/day)	Retention time (hours)	Temp. (°C)	Effluent	
			pH	Zn^{2+} (mg/L)
10	24	30	6.21-8.01	0.09-0.82
20	12	30	6.19-6.53	0.14-0.30
40	6	30	6.14-6.78	0.08-1.47
80	3	30	6.23-7.00	0.10-0.68
40	6	20	6.20-7.00	0.03-0.31
40	6	15	6.50-6.71	0.13-0.18
80	3	15	6.40-6.60	0.16-0.26

(3) Concentration of the bacteria typically ranged from about 4-5X10^9 cells/mL throughout the experiment.

PILOT PLANT-SCALE TEST

Materials and Methods

A pilot plant-scale test was performed at Yanahara Mine in the Okayama Prefecture, based on the results of the laboratory experiment.

The test was in a continuous flow process using a fluidized bed-type anaerobic reactor with a working volume 180L, which was scaled-up version of the laboratory experiment system.

A schematic diagram of the plant and flow diagram of the process used are illustrated in figure 2 and figure 3, respectively.

The culture of the bacteria used for the test was the same as the previous laboratory experiment.

Mine drainage of Yanahara Mine, the quality of which is shown in table 3, was supplemented with sodium lactate, yeast extract, and inorganic materials. This mixed water was fed to the anaerobic reactor.

As the raw drainage was too acidic(pH 2.50-2.65) to maintain the activity of the bacteria and to clear the emission standard, the drainage was controlled by adding powdered limestone, the average grain size of which was 1.1 micrometer, to maintain pH at about 5 before the mixing. The condition of the influent is shown in table 4.

Table 3.--Chemical characteristics of mine drainage from the Yanahara Mine used for the pilot-plant scale test.

Component	Value
temperature	20°C
pH	2.5-2.65
Fe^{2+}	171-303 mg/L
Total-Fe	693-815 mg/L
Zn^{2+}	41.5-52.1mg/L
Cu^{2+}	9.4-16.8mg/L
Cd^{2+}	0.18mg/L
Mn^{2+}	7.4 mg/L
Total-As	0.21mg/L
Acidity as $CaCO_3$	1,991-2,442mg/L

Table 4.--Condition of the feed water used throughout the pilot plant-scale test.

Temperature (°C)	Inflow (L/day)	Yeast extract (g/L)	Na-lactate (g/L)	pH	Period (days)
24.7-30.2	180	0.5	3.5	6	16
25.8-28.8	360	0.25	3.5	6	2
22.2-27.7	360	0	3.5	5	12
19.0-25.6	720	0	3.5	5	13
18.1-22.8	720	0	3	5	8
14.8-19.8	720	0	2.5	5	10
10.0-16.2	720	0	2	5	20
10.8-14.9	720	0	1.5	5	18
9.0-14.2	720	0	1	5	14

The test was made increasing feed volume at three steps, 180, 360 and 720 L/day and was performed for 113 days continuously.

Sodium lactate and yeast extract were reduced from 3.5g/L to 1.0g/L and 0.5g/L to zero, respectively. Temperature in the reactor ranged between 9.0°C and 30.2°C, depending on the weather, because the test plant was not housed in order to test the procedure in practical use too.

Excess hydrogen sulfide except for the volume, which was bubbled into the reactor, was vented.

The COD in the effluent was measured by the dichromate titration.

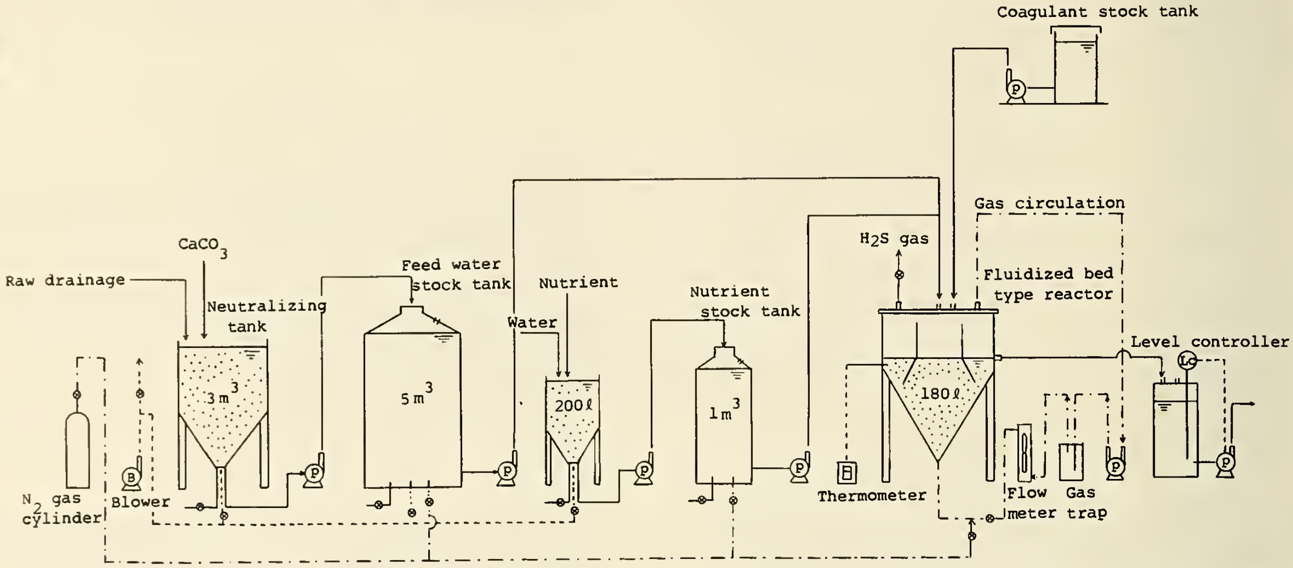
Coagulant stock tank
Gas circulation
H_2S gas
Fluidized bed type reactor
Level controller
LC
$CaCO_3$
Raw drainage
Neutralizing tank
Feed water stock tank
Nutrient
Water
Nutrient stock tank
$3 m^3$
$5 m^3$
200 ℓ
$1 m^3$
180 ℓ
P
B
N_2 gas cylinder
Blower
Thermometer
Flow meter
Gas trap

Figure 2.--Diagram of drainage treatment system used in the pilot plant-scale test.

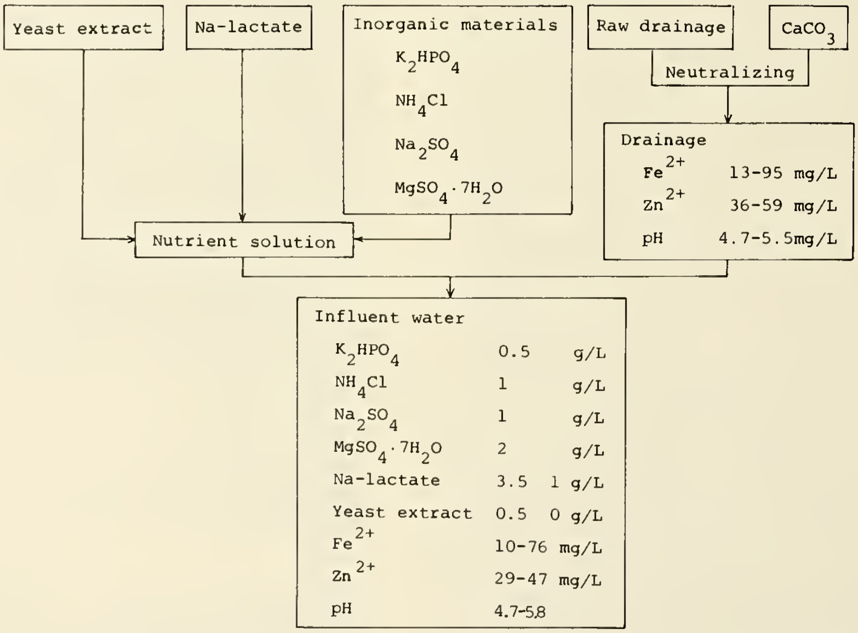
Yeast extract
Na-lactate
Inorganic materials
K_2HPO_4
NH_4Cl
Na_2SO_4
$MgSO_4 \cdot 7H_2O$
Raw drainage
$CaCO_3$
Neutralizing
Drainage
Fe^{2+} 13-95 mg/L
Zn^{2+} 36-59 mg/L
pH 4.7-5.5mg/L
Nutrient solution
Influent water
K_2HPO_4 0.5 g/L
NH_4Cl 1 g/L
Na_2SO_4 1 g/L
$MgSO_4 \cdot 7H_2O$ 2 g/L
Na-lactate 3.5 1 g/L
Yeast extract 0.5 0 g/L
Fe^{2+} 10-76 mg/L
Zn^{2+} 29-47 mg/L
pH 4.7-5.8

Figure 3.--Flow diagram of feed water in the pilot plant-scale test.

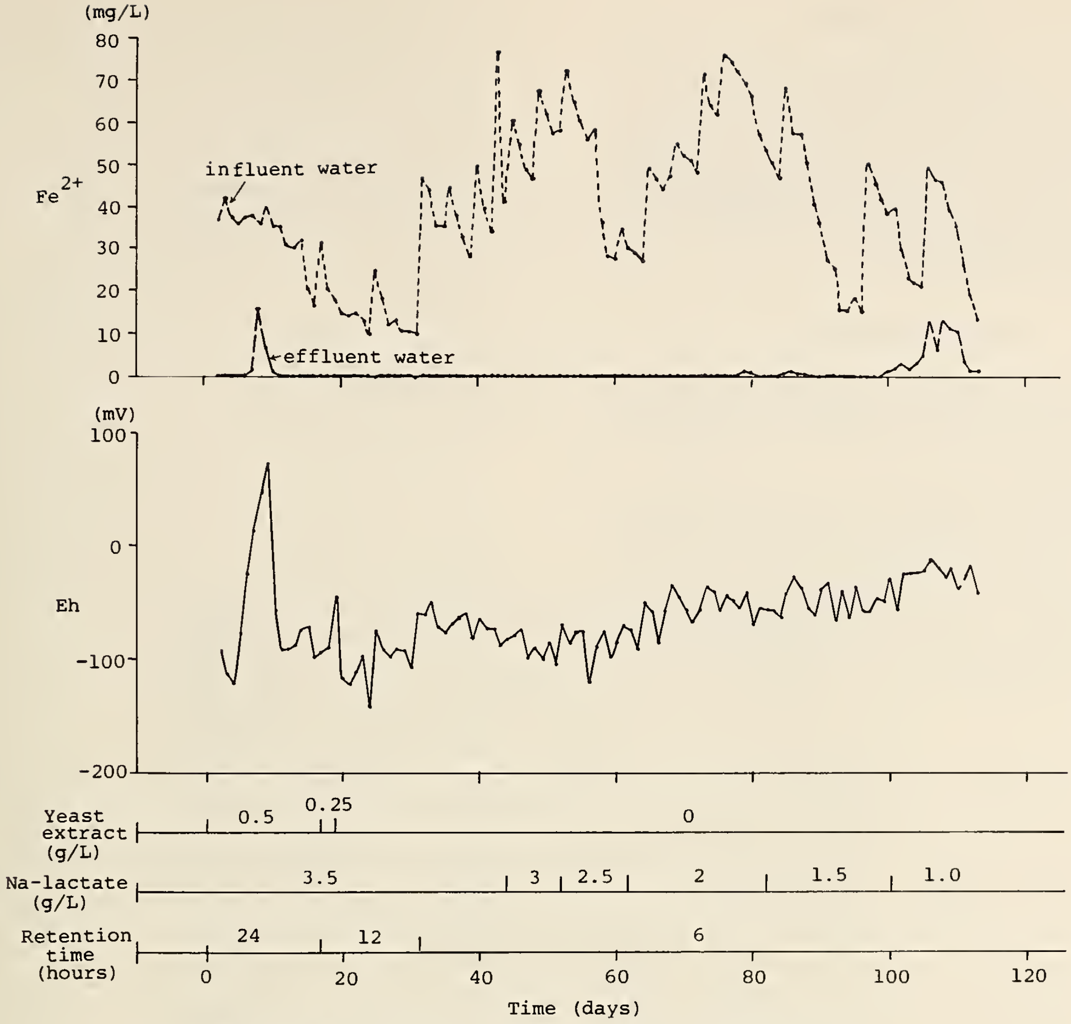

Figure 4.--Result of pilot plant-scale test.

Results

Most of the metals in the mine drainage were separated into precipitate of sulfides consistently as was the case in the laboratory experiment. The results of the test are shown in figure 4. The Fe^{2+} and Zn^{2+} ions in the feed water were reduced to $Fe^{2+} < 1.0$mg/L, $Zn^{2+} < 0.2$mg/L, below the emission standards in Japan, except for the period of the start-up and the very last stage. The cause of the increasing Fe^{2+} in the effluent at the start-up is not known. The same phenomenon at the end of the experiment was clearly due to the decreasing of Na-lactate. The COD in the effluent, however, was 800-1,000mg/L throughout the test, which is over the standard.

The followings was concluded from the results of the pilot plant-scale test.

(1) A cut in the amount of yeast extract was possible

(2) Mine drainage with chemical quality of Fe^{2+} 40mg/L, Zn^{2+} 40mg/L and pH4.7 was treated successfully at 12°C, sodium lactate level at 1.5g/L, and retention time of 6 hours(720L/day inflow)

(3) Concentration of the bacteria remained at from 4-5X10^9 cells/mL as same as was in the laboratory experiment.

CONCLUSIONS

A continuous flow test of a biological method for treatment of mine drainage at Yanahara Mine showed that most of the metals in the mine drainage can be reduced in a pilot plant-scale process when suitable organic carbon for sulfate-reducing bacteria is supplied, and inflow and temperature of the reactions are properly controlled.

However, the following problems must be solved to complete a system for practical use:

(1) The COD value in the effluent must be decreased to within the emission standard

(2) Cheaper nutrients must be selected in order to hold cost down.

ACKNOWLEDGEMENT

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GROWTH RESPONSES AND IRON UPTAKE IN SPHAGNUM PLANTS AND THEIR RELATION TO ACID MINE DRAINAGE TREATMENT[1]

Anne Kearney Spratt and R. Kelman Wieder[2]

Abstract.-- Increasing interest in the use of Sphagnum wetlands to treat acid mine drainage (AMD) has prompted study of the tolerance of Sphagnum species to the various constituents of AMD waters. In this study, S. fallax and S. henryense plants were grown in the laboratory for 33 days in synthetic bog water to which $FeCl_2$ was added to achieve Fe^{2+} concentrations ranging from 0 to 10,000 mg/L. Upon exposure to Fe concentrations $\geq$ 100 mg/L, both species exhibited a significant reduction in growth after 33 days relative to controls, but this reduction was proportionately less for S. fallax than for S. henryense. Final Fe concentration in the plant tissue was negatively correlated with growth and chlorophyll concentration in both species, and greatly exceeded the total cation exchange capacity for Sphagnum, suggesting nutrient cation deficiency as a mechanism of Fe toxicity. Based on data from a previous study of net primary productivity of Sphagnum species in Big Run Bog, estimates were made for Fe accumulation by the growing plants on an areal basis. Projected areal accumulation of Fe was greatest at high Fe treatment concentrations (1,000-10,000 mg/L) for both species, despite significant decreases in plant growth. These estimates reinforce the conclusion that Fe uptake by growing Sphagnum plants can play only a relatively minor role in Fe retention in wetland systems constructed for mine drainage treatment. Results of this study also indicate that the viability of Sphagnum wetlands constructed for AMD treatment may be dependent on the species composition.

INTRODUCTION

As a result of several studies suggesting that chemical and biological processes in freshwater wetlands may remove acidity, sulfate, and heavy metals from acid coal mine drainage (Wieder and Lang 1982, Kleinmann et al. 1983, Burris et al. 1984, Tarleton et al. 1984, Wieder and Lang, 1984, Gerber et al. 1985, Wieder et al. 1984a, 1985, McHerron 1986, Brodie et al. 1987), there has been an increasing interest in using constructed wetland systems as a low-cost, low-maintenance alternative to traditional chemical treatment of acid mine drainage (AMD). Before the wetland approach to AMD treatment becomes feasible, however, the effects of AMD on wetland vegetation, including *Sphagnum*, must be evaluated. The vegetation in man-made wetland systems serves not only as a mechanism of metal retention by the process of plant uptake, but also as a mechanism of stabilization of the organic substrate within the wetland, minimizing the potential for erosion.

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Under natural conditions, *Sphagnum* growth and species distributions are affected by environmental factors such as pH, moisture, and nutrient availability (Clymo 1973, Vitt et al. 1975, Andrus et al. 1983, Titus et al. 1983, Wagner and Titus 1984, Andrus 1986). *Sphagnum* species can accumulate Fe and other metals with no apparent inhibition of growth when subjected to chronic inputs of low concentrations of metals via atmospheric deposition (Pakarinen and Tolonen 1976, Pakarinen 1978, Aulio 1980, Lembrechts and Vanderborght 1985). Accumulation under these conditions is species specific (Aulio 1982) and is not necessarily correlated with plant growth (Pakarinen and Rinne 1979).

In contrast to the considerable amount of information available on *Sphagnum* growth in relatively undisturbed environments, comparatively little is known about the response of *Sphagnum* to the low pH and high metal concentrations typical of AMD. One study has demonstrated that the discharge of chemically treated mine drainage (pH values from 6 to 9) into what was once a naturally acidic *Sphagnum* wetland (surface water pH near 4.0) resulted in both the death of the vegetation and erosion of the organic peat down to the underlying mineral soil (Wieder et al. 1984b).

In light of these findings, the objectives of this study were to assess the growth responses of two commonly occurring *Sphagnum* species in solutions with Fe concentrations typically found in AMD, and to assess the apparent uptake of Fe from solution by these two *Sphagnum* species. Also, the potential contribution that uptake of Fe by growing *Sphagnum* could make to Fe retention within a wetland is compared to the potential contribution that other chemical and biological processes could make to Fe retention.

METHODS

Living plants of two *Sphagnum* species, *Sphagnum fallax* and *S. henryense*, were collected at Big Run Bog, WV, a *Sphagnum*-dominated wetland not affected by AMD. In the laboratory, individual plants of each species were cut to an initial length of 5 cm and placed in groups of 7 or 8 into 2.5-cm-diameter, 3.5-cm-tall PVC cylinders (Wieder et al. 1984b). Three of these cylinders were placed in an 8-cm-diameter fingerbowl to which a particular treatment solution was added. Treatment solutions contained either 0, 1, 10, 100, 1,000, or 10,000 mg/L Fe, thereby spanning the range of Fe concentrations typical of AMD (Braunstein et al. 1977). Ferrous chloride, rather than $FeSO_4$, was used in preparing the treatment solutions. A previous study of the growth of *S. fallax* and *S. henryense* in AMD waters demonstrated that growth was negatively correlated with SO_4^{2-}, but not with Cl^-, concentrations in AMD (Kearney, 1986). The treatment solutions were prepared by adding $FeCl_2$ to synthetic bog water containing, in mg/L: 0.88 Ca^{2+}, 0.19 Mg^{2+}, 0.47 K^+, 0.23 Na^+, 0.16 NH_4^+, 0.07 NO_3^-, 3.44 SO_4^{2-}, and 0.62 Cl^-. The synthetic bog water approximates the ion concentrations found in Big Run Bog surface waters (Wieder 1985). Treatment solutions were added to each bowl so that the water table was at the tops of the PVC cylinders. Every 2-3 days, additional treatment solution was added to maintain the water at the tops of the cylinders, and at weekly intervals the entire volume of water in each bowl was replaced. Plants were grown for 33 days beginning on December 23, 1985, for *S. fallax* and on January 8, 1986, for *S. henryense*.

Plant growth was assessed by removing individual plants from their cylinders and measuring their length with a metric ruler at 11-day intervals. Since growth of *Sphagnum* is indeterminate and occurs along the long axis of the plant, increase in length is an appropriate measure of growth over time (Clymo 1970).

After 33 days, determinations of chlorophyll concentration were made. Using approximately half of the plants from each bowl, the uppermost 1 cm of tissue (capitulum) was excised and weighed. Chlorophyll was extracted from the fresh plant tissue with 80% aqueous acetone (Dolphin 1978). Absorbance of the extract at 649 and 665 nm was measured using a double-beam spectrophotometer, and chlorophyll concentration was calculated using equations given in Dolphin (1978).

The plants remaining in each bowl were weighed and then dried for 24 hours at 55° C for fresh mass/dry mass ratio determinations. The dried plant material was ashed in a muffle furnace at 300° C for 1 hour and at 800° C for 3 hours. The ash was extracted with 6 M HCl and brought to final volume with distilled water (Likens and Bormann 1970). Iron concentrations in the extract solutions were determined by atomic absorption spectrophotometry. For more detailed methodology, see Kearney (1986).

For each species, effects of Fe concentration in the treatment solution on growth (increase in length over the 33-day period) and chlorophyll concentration were assessed using Friedman's tests conducted on the data from day 33. Correlations between growth, final chlorophyll concentration, final tissue Fe concentration, and Fe concentration in the treatment solutions were determined using Spearman's rank correlation tests. Differences between the species with regard to growth and final tissue Fe concentration were evaluated with Mann-Whitney tests. A significance level of p=0.05 was used in all tests.

RESULTS

The two Sphagnum species exhibited both similarities and differences in growth responses to increasing Fe in the treatment solutions. For S. fallax, after 33 days growth in the 1 mg/L Fe solution was significantly greater than that in the control solution (0 mg/L), and growth in the 10 mg/L Fe solution did not differ significantly from that in the control solution. However, as solution Fe concentrations increased from 100 to 10,000 mg/L, plant growth progressively decreased (fig. 1). In contrast, for S. henryense growth at all Fe concentrations was significantly less than growth in the control solution (fig. 2). For each species, the increase in length achieved over 33 days was significantly negatively correlated with treatment solution Fe concentration (Spearman's rho values of -0.82 and -0.93 for S. fallax and S. henryense, respectively). Also for both species, at solution Fe concentrations $\geq$ 100 mg/L not only was growth reduced relative to controls, but also no significant increase in growth was observed after the first 11 days. Regardless of treatment solution Fe concentration, the inhibition of growth relative to control plants was proportionately greater for S. henryense than for S. fallax (fig. 3).

Final chlorophyll concentration in S. fallax generally decreased with increasing treatment solution Fe concentration (fig. 1). For S. henryense, final chlorophyll concentration in treatment solution Fe concentrations $\leq$ 10 mg/L were not significantly different from those plants grown in 0 mg Fe/L, but as Fe concentrations in treatment solutions increased to 100 mg/L and greater, chlorophyll concentration decreased (fig. 2). In each species, chlorophyll concentration in plant tissues after 33 days was positively correlated with increase in length (Spearman's rho values of 0.68 and 0.82 for S. fallax and S. henryense, respectively). Moreover, at

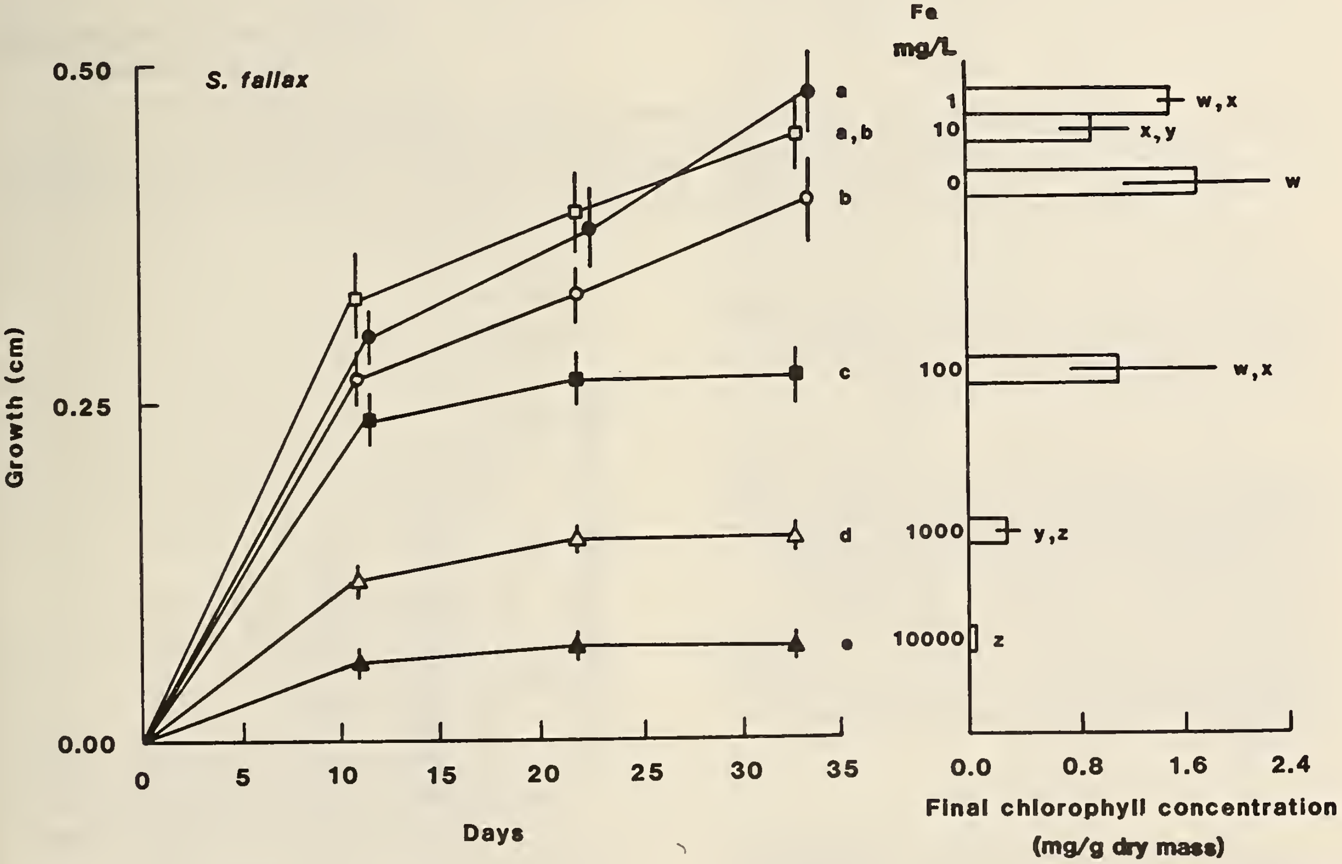

Figure 1.--Growth and final chlorophyll concentration of Sphagnum fallax in Fe solutions. (For growth, each symbol represents the arithmetic mean of 72 values ± 1 standard error. Values for mean length after 33 days with the same letter (a-e) do not differ significantly. For chlorophyll concentration, the mean and range of 3 measurements are shown. Values with the same letter (w-z) do not differ significantly. Iron concentrations in the treatment solutions are indicated to the left of the chlorophyll bars).

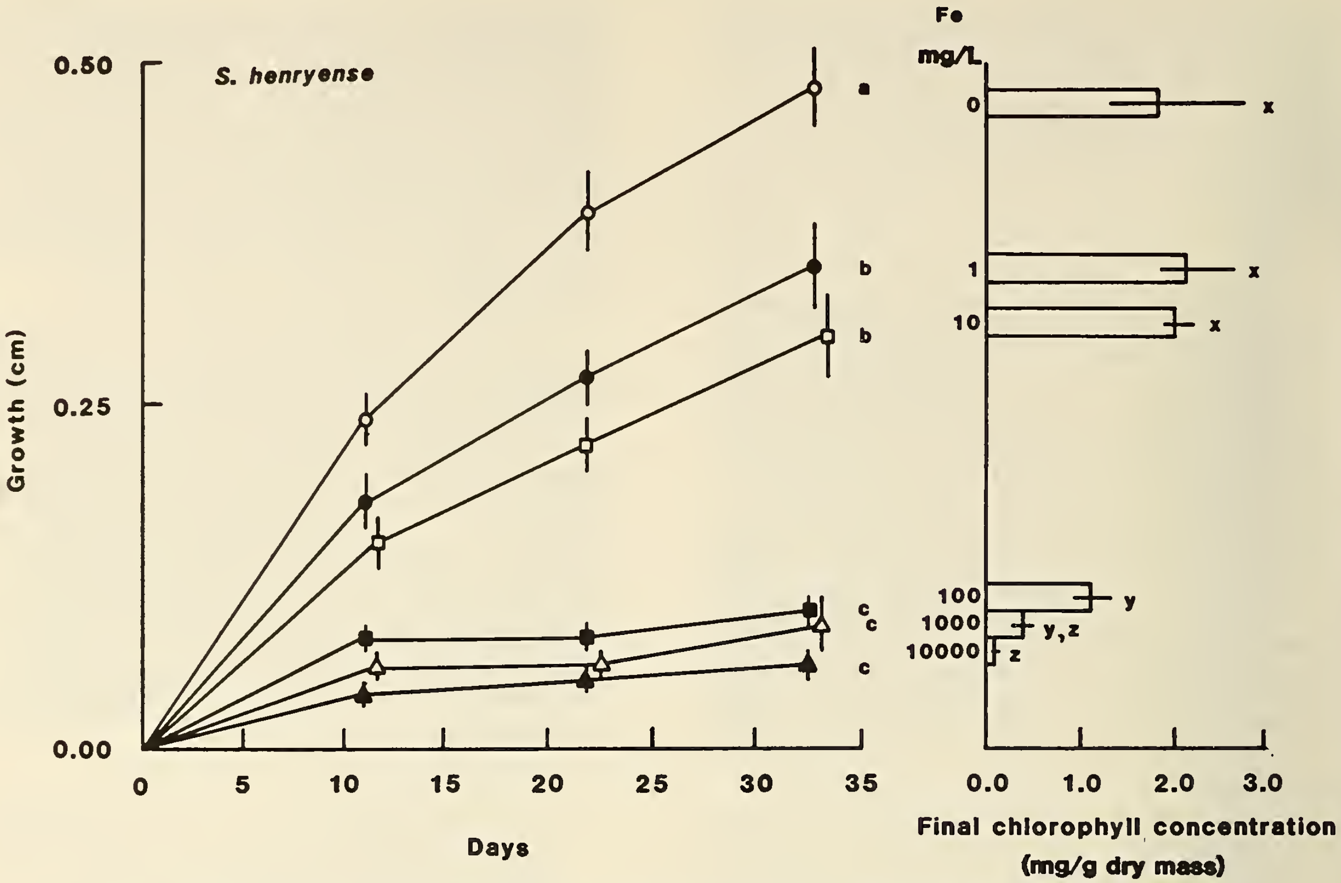

Figure 2.--Growth and final chlorophyll concentration of Sphagnum henryense in Fe solutions. (For growth, each symbol represents the arithmetic mean of 63 values ± 1 standard error. For chlorophyll concentration, the mean and range of 3 measurements are shown. For explanation of letter symbols, see Figure 1 legend. Iron concentrations in the treatment solutions are indicated to the left of the chlorophyll bars.)

Fe concentrations ≥ 100 mg/L, final chlorophyll concentration was less than 1.2 mg/g dry mass and no additional growth was achieved after the first 11 days.

For both species, Fe concentration in the plant tissues after the 33-day period increased with increasing treatment solution Fe concentration (fig. 4), yet there was no significant difference between the two species in final tissue Fe concentration across all treatment solution Fe concentrations (p=0.34). For each species, growth achieved after 33 days was negatively correlated with final tissue Fe concentration (Spearman's rho values of -0.83 and -0.86 for S. fallax and S. henryense, respectively).

DISCUSSION

The observed reduction in Sphagnum growth with increasing Fe concentration in the treatment solutions may be related to a decreased ability of the plants to take up nutrient cations. Cation exchange on the cell walls of Sphagnum plants appears to be a major mechanism of cation uptake by the living cells of the plants (Clymo 1967). The maximum reported values for

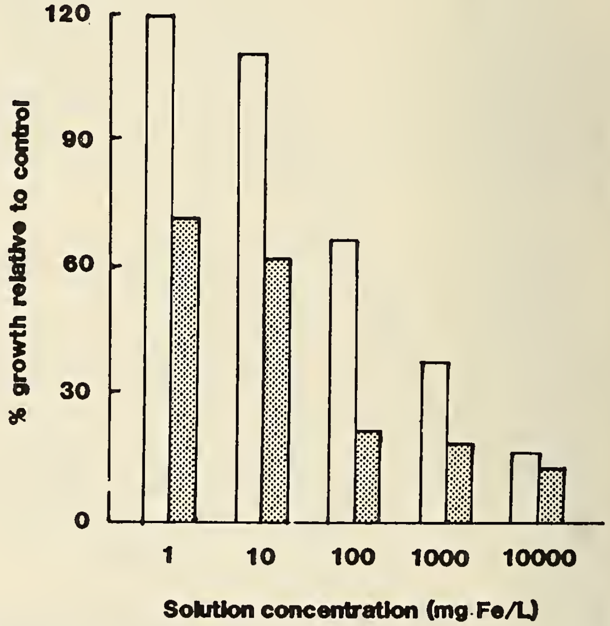

Figure 3.--Mean growth after 33 days of Sphagnum fallax (open bars) and S. henryense (stippled bars) in Fe solutions, expressed as percent relative to control treatments (0 mg Fe/L).

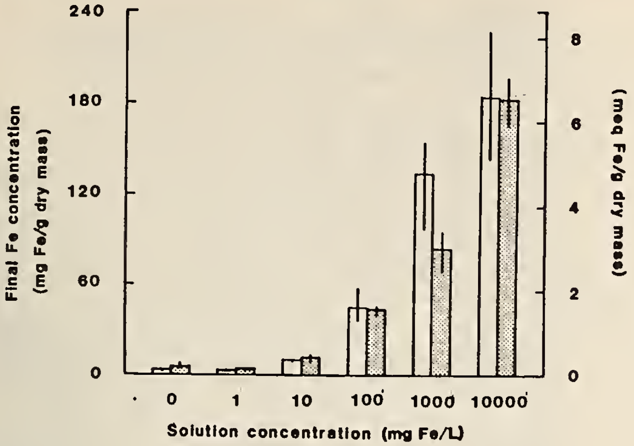

Figure 4.--Final concentrations of Fe in the tissues of *Sphagnum fallax* (open bars) and *S. henryense* (stippled bars). The arithmetic mean and range of 3 measurements are shown.

cation exchange capacity in *Sphagnum* species are close to 1 meq/g dry mass (Clymo 1967, Spearing 1972), and base saturation of *Sphagnum* (percent of total cation exchange capacity accounted for by the base cations Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) has been measured as 8.7% (Braekke 1981). Cation exchange is a dynamic process in which equilibria between adsorbed cation and soluble cation concentrations are rapidly established (Clymo 1963). Therefore as Fe^{2+} concentration in solution increases, increasing quantities of base cations and protons will be desorbed from exchange sites because of competition from the Fe^{2+} ions. For both *Sphagnum* species, when grown in solutions with Fe concentrations $\geq$ 100 mg/L, not only did final Fe concentration in the plant tissues exceed the cation exchange capacity of *Sphagnum* (1 meq/g dry mass; cf. fig. 4), but also a dramatic reduction in both growth and chlorophyll concentration relative to controls was observed after 11 days (figs. 1,2). Thus, the observed reduction in plant growth may have been a result of a deficiency of nutrient base cations induced by competition from Fe^{2+} for exchange sites.

The concentration of Fe in the tissues of both species exceeded the total cation exchange capacity of the plants by as much as 650% in Fe treatment solution concentrations $\geq$ 100 mg/L (fig. 4). This excess Fe must have been incorporated into the plants as nonexchangeable Fe via specific binding to organic matter or by the formation of Fe oxides or oxyhydroxides (cf. Wieder et al. 1987). No obvious oxide deposits were discernible during examination of the tissues using light or scanning electron microscopy, suggesting that organic binding of Fe by the plants may have been a more important process in Fe accumulation than either cation exchange or oxide formation.

The potential contribution of growing *Sphagnum* plants to Fe retention in a wetland constructed for AMD treatment can be estimated based on the growth of the plants relative to controls (fig. 3) and measured Fe uptake (fig. 4). To estimate potential Fe uptake on an areal basis, field estimates of primary productivity of *Sphagnum* must be incorporated into the computation. The average annual net primary productivity of the two dominant *Sphagnum* species from Big Run Bog (*S. fallax* and *S. magellanicum*) is 5.75 g dry mass/dm^2/yr (Wieder and Lang 1983). Multiplying this value by the percent growth relative to controls (from fig. 3) and by final tissue Fe concentration (from fig. 4) for each species at each solution Fe concentration yields estimates of potential Fe accumulation by growing *Sphagnum* (table 1). The projected areal accumulation of Fe by *S. fallax* was 30 to 230% greater than that by *S. henryense* for any particular solution Fe concentration. This difference is accounted for by the difference between the species in growth relative to controls; in all solution Fe concentrations excluding 10,000 mg/L, reduction of growth of *S. fallax* was significantly less than the reduction of growth of *S. henryense* (fig. 3). The maximum Fe accumulation projected for the two species (29 g/m^2/yr) was more than 8 times greater than a previous estimate (3.5 g/m^2/yr) based on a lower Fe concentration in *Sphagnum* tissue (5.8 mg/g; Wieder et al. 1987). However, in achieving an Fe uptake value of 29 g/m^2/yr, the plants would be effectively dead. At Fe treatment solution concentrations at which plants were still growing and green, maximum Fe uptake is only 6.5 g/m^2/yr. Despite these new estimates of the potential maximum for Fe uptake by *Sphagnum* plants, the contribution that plant uptake would make to total Fe retention in a wetland system is still small in comparison to the contributions made by other chemical and biological processes within the peat, especially the binding of Fe to

Table 1.--Estimation of the potential Fe uptake, on an areal basis, by growing *Sphagnum* plants subjected to different Fe concentrations in AMD. Methods used to make these estimates are described in the text.

Treatment Solution Fe Concentration (mg/L)	Estimated Fe uptake (g/m^2/yr)	
	S. fallax	*S. henryense*
1	2.2	1.8
10	6.5	4.1
100	16.8	5.4
1000	29.0	8.8
10000	17.7	13.8

organic matter and the formation of Fe oxides, which together may account for as much as 97% of total Fe retention (Wieder et al. 1987).

These results show that Sphagnum plants can survive and grow in solutions with Fe concentrations up to 10 mg/L, but at 100 mg/L or greater, they turn brown and stop growing. In a wetland designed to treat low flows of AMD containing relatively low Fe concentrations, the plants could remain viable. In addition, although Sphagnum plants do accumulate more Fe when exposed to higher Fe concentrations, the potential contribution of Sphagnum plants to overall Fe retention in comparison to other processes contributing to Fe retention in a wetland constructed for AMD treatment appears to be minor. Nonetheless, the need to maintain a vigorous cover of vegetation in constructed wetland treatment systems is critical in terms of minimizing the potential for erosion of an organic substrate. We have demonstrated clear differences between species in their growth and chlorophyll responses to AMD; S. fallax would exhibit greater increase in length than S. henryense in Fe-rich water. Further study of Sphagnum species responses to other AMD constituents, particularly to metals, is warranted to determine which species of Sphagnum are most likely to survive when exposed to different types of AMD.

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AN OVERVIEW OF THE ROLE OF ALGAE IN THE TREATMENT OF ACID MINE DRAINAGE[1]

D. A. Kepler[2]

Abstract.--Preliminary studies utilizing the digestion and ashing of freshwater algae of several phyla, samples from acid mine drainage (AMD) sources, indicate relatively high concentrations of iron and manganese associated with the algae. A wetland treatment system was constructed in September 1987 at an abandoned drift mine in Pennsylvania, associated with the Lower Clarion Coal Seam. In this system, specifically designed and planted "algae ponds" are integrated with emergent marsh sections of the system in an effort to examine the role of algae in treating AMD. The site of mineral accumulation in the algae (adsorbed and/or intracellular concentrations) and the form(s) in which the minerals are found in the algae are of primary interest. The relationship between iron and manganese regarding uptake in the cells, the life histories and possible succession of predominant algae species in the ponds, the correlation between mineral uptake and water quality, the effects of mineral toxicity to the algae, and the potential ability of algae to modulate effluent pH values on a diel basis will also be investigated. An overview of methods and their rationale along with results to date at the noted study site will be presented, with the intent of allowing for the replication and expansion of the study by others.

INTRODUCTION

Freshwater algae are common and widespread inhabitants of the waters associated with coal mine drainage and are recognized as being effective accumulators of metals (Bates et al. 1982, Crist et al. 1981, Wetzel 1975). The majority of work related to algae and the bioaccumulation of metals has typically been with metals that are generally of little concern, from a regulatory standpoint, in coal mine drainage, notably zinc, nickel, copper, and lead.

Iron and manganese, however, are probably the two most common, and regulated, mineral constituents of mine drainage, accounting for millions of dollars in chemical treatment costs annually. Iron, which is relatively easy to remove from mine drainage, presents few logistical problems to chemical treatment, but manganese is a more persistent mineral and requires rather sophisticated treatment to achieve effluent standards. Additionally, concentrations of 50-100 mg/L of manganese are not uncommon in acidic mine drainage (Patterson 1975).

Algae require iron and manganese as essential micronutrients. Although concentrations of manganese > 1 mg/L have been shown to be inhibitory to some blue-green and green algae (Gerloff and Skoog 1957, Patrick et al. 1969), algae are commonly found and often abundant in AMD with high concentrations of iron and manganese. Algae associated with these areas have been shown to accumulate manganese, with reported levels of manganese as high as 56,000 mg/kg of plant tissue

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(dry weight) (Kepler 1986). This is of particular interest in that biological treatment systems, i.e., man-made wetlands, are proving to be a viable and cost-effective means of treating AMD.

To date, most man-made wetlands are constructed as Sphagnum-dominated, or more commonly, Typha-dominated treatment systems (Kleinmann and Girts 1986). Algae are generally not purposefully introduced into these wetlands, but become established in the systems by way of the source of the mine drainage, the air, soil, and most commonly, in association with the principal, transplanted wetland vegetation. Because of this secondary nature of establishment, any beneficial effects of algae on the quality of AMD often go unrecognized, or the beneficial effects are limited because the Wetland Treatment System (WTS) is not designed to optimize algal habitat and therefore, algal biomass is limited. Little is actually known concerning the role algae has in the treatment of AMD in these Wetland Treatment Systems.

This paper is intended to be an overview of work in progress concerning the role of algae in the treatment of AMD in WTS's, with particular emphasis placed on the mechanisms involved in the bioaccumulation of manganese, Construction of the study WTS began in September of 1987, and therefore, limited findings are available at this time. However, the objectives and methods of the study, along with any results to date, will be reported and discussed.

DESCRIPTION OF RESEARCH

Background

This study is being funded by the United States Department of the Interior, Bureau of Mines, under the Abandoned Mine Land research program and is listed as, "Acid Mine Drainage Treatment Utilizing Blue-Green Algae." The study wetland is located in Richland Township, Venango County, PA, and was constructed in cooperation with Glacial Minerals, Inc., of Strattenville, PA, on land owned and previously surface mined by Glacial Minerals, Inc. The source of the acid mine drainage being treated by the WTS is from an abandoned drift mine (circa 1920) that has been discharging since at least 1940 and is now considered to be receiving recharge waters from the adjoining surface mine. The water is associated with the Lower Clarion Coal Seam and flows at an average of 37 gal/min. The AMD quality at the source is characterized as follows: pH, 5.0; alkalinity, 16 mg/L; mineral acidity, 450 mg/L; total iron, 130 mg/L; manganese, 71 mg/L; aluminum, 4 mg/L; and sulfate, 2,200 mg/L.

Construction

Construction began in September of 1987 with the majority of the system completed by November of that year. The WTS was designed and built with an initial collection pond immediately adjacent to the drift mine source, followed by two, distinct, parallel wetlands. The two wetlands combine at their respective outflow points and flow through a planted ditch to a conventional treatment pond series.

The parallel wetlands are set up as four individual units in each system, two shallow (6-12 in), Typha-dominated ponds followed by two, deeper (3-4 ft) algae-dominated ponds in one series; and two algae ponds followed by two Typha ponds in the other series. Each pond has an approximate surface area of 600 ft^2 and is connected to the next pond in series by a section of 6-in diameter plastic pipe. The system is graphically displayed in figure 1.

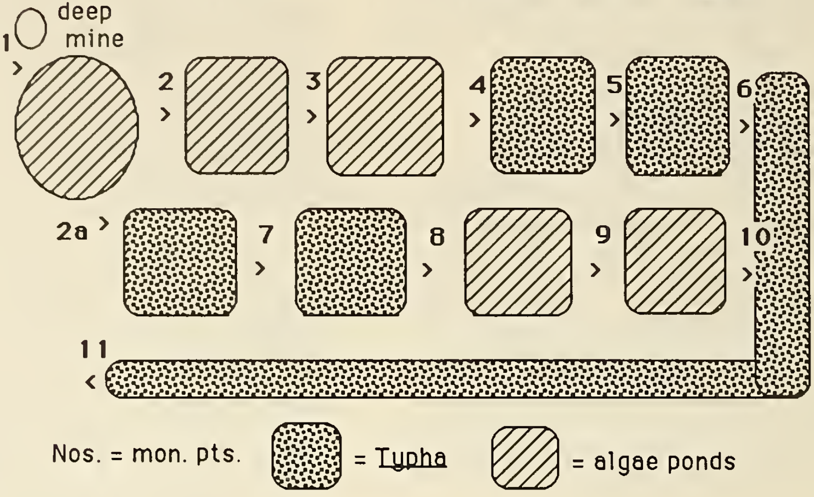
The ponds were constructed with available, on-site clay and a 12-in base of composted manure which serves as a planting medium and a source of nutrients to the vegetation. Four to six inches of agricultural limestone was placed beneath the compost in the final, planted ditch, but no alkaline materials were used in any other portion of the wetland. Typha latifola was available on site, and was hand dug and planted at a density of roughly one mature plant and rhizome mass per 2 ft^2. Scirpus cyperinus and Juncus effusus were also available on site and were introduced in the Typha ponds primarily in the areas of the inflow/outflow pipes. S cyperinus and J. effusus were also planted around the edges of the algae ponds to stabilize the banks and to provide possible sites of attachment for algae.

Initially, the study intended to concentrate on blue-green algae (Cyanobacteria) of the genus Oscillatoria. Oscillatoria spp. was noted as being prevalent in several natural and man-made wetlands that displayed reductions in manganese levels from source to outflow, and was the species noted above exhibiting manganese levels of 56,000 mg/kg of plant. However, during the period between the original proposal and the actual planting of the study wetland, the predominant algae in the previously Oscillatoria-dominated wetlands became the green algae of the genus Mougeotia. Oscillatoria was still present, but not dominant.

The water quality in these wetlands continued to show manganese reductions, and analysis of Mougeotia samples confirmed that they too were accumulating manganese. Therefore, the decision was made to transplant algae from one of these sources into the study WTS, knowing that the predominant algae being "planted" was Mougeotia, but that Oscillatoria was also being introduced at the study site. Approximately one 30-gal container of Mougeotia-dominated algae was introduced into each of the four algae ponds at the study wetland. Because the side of the parallel series with the Typha ponds down-flow of the algae ponds would be immediately affected by this planting and the other side would not be affected, a container of algae was also introduced into each of the four Typha ponds.

Various other species of algae, primarily diatoms, were also introduced into the wetland with the principal algae planting, and a filamentous green algae was noted as being associated with the Typha planting. These species, while of little apparent significance regarding total numbers at the time of the planting, are being identified and may be found to take on some degree of importance in treatment during the 1988 growing season.

Figure 1.--Plan view of wetland treatment system.



Water Analysis

The AMD source, the inflow/outflow for each pond, and the final outflow point of the wetland have been designated as water monitoring points in this study. Each monitoring point will be sampled weekly over the 18-month study which began in September of 1987. The samples are analyzed for pH (electrometrically); specific conductance (μ mhos at 25° C); alkalinity and mineral acidity (titrimetrically at pH 4.5 and 8.3 respectively); and total and ferrous iron, total and dissolved (dissolved: passing a 45-μ membrane filter) manganese, and sulfate and aluminum (all minerals are determined spectrophotometrically). Water temperatures (° C) are taken from each pond in the field at the time of collection. All analyses are conducted following the Standard Methods for the Examination of Water and Wastewater and are done in accordance with E.P.A. guidelines.

Flows are measured weekly by means of a portable cutthroat flume in the channels and by bucket and stopwatch at the discharge pipes. In this manner, the total water budget of the WTS may be known, with any increases or decreases in the system readily noted.

Vegetation Analyses

Representative samples of the wetland vegetation will be collected and analyzed for iron, manganese, and aluminum content beginning in the spring of 1988 and then periodically throughout the study, with principal concern given to the predominant algae species. Total metals are determined as follows: the samples are dried, ashed by means of heating at 550° C in a muffle furnace for two hours, acid digested by standard methods, and analyzed for mineral concentrations by atomic absorption. Results are reported as mg of mineral/kg of plant (dry Weight).

To determine the site of mineral accumulation in the algae, i.e., adsorbed and intracellular concentrations, the algae samples are "washed" with an EDTA solution in a shaker bath and then filtered. The extract is analyzed by atomic absorption to determine the concentration of adsorbed mineral associated with the algae. The "washed" algae is then ashed and analyzed as described above to determine the intracellular concentration of minerals.

The form of the minerals in and on the algae, e.g., adsorbed manganic oxide, will also be determined utilizing a form of x-ray diffraction so as to predict the long-term stability of the minerals in the wetland and the mechanisms of accumulation.

Diurnal studies will be conducted during periods of accelerated algal growth to examine the dissolved oxygen content and pH of the ponds and, therefore, whether the algal blooms have any effect on pH values. Carbon dioxide removal and production in the wetland, through algal photosynthesis and respiration, can account for shifts in pH values, although this phenomenon is generally associated with alkaline waters (Cole 1979). Lake pH's in western Pennsylvania have been noted to fluctuate five pH units over a 24-hr period due to the effects of blue-green algal blooms (Kepler 1985).

RESULTS AND DISCUSSION

Water

At the time of this writing, water quality data are available for the last two weeks of September 1987, through the first two weeks of January 1988. The numbers reflect the effects of a newly planted, somewhat dormant wetland. The Typha planting died back early in September simply because of the season, and the algae populations have not had favorable weather conditions to bloom. However, between the compost and the dead vegetation there is considerable organic matter present in the WTS, the rhizomes in the Typha ponds are active, bacteria and algae are present in the system, and the WTS is designed to maximize plant contact and retention time with the flows. Therefore, even at this early date, positive water quality results can be seen (figures 2-5).

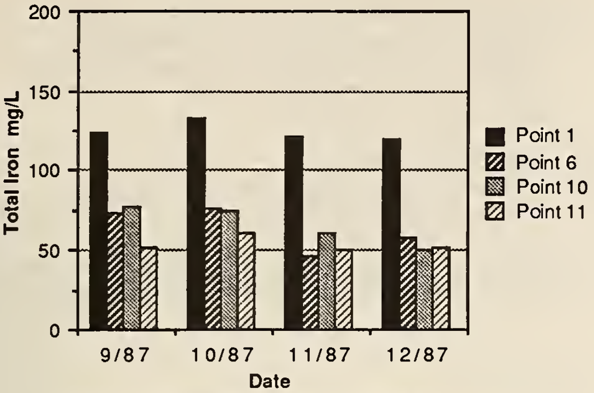


Figure 2.--Average total iron at AMD source, points 6 & 10, and final outflow.

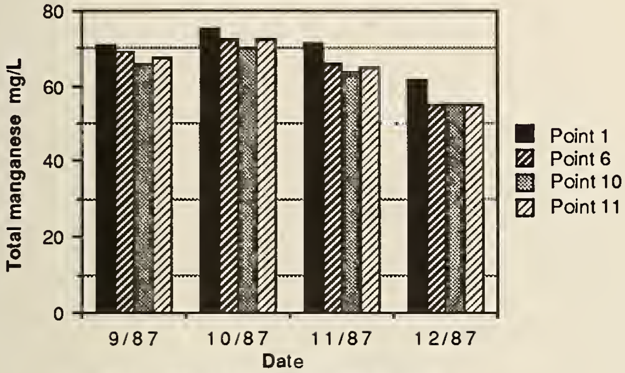


Figure 3.--Average total manganese at AMD source, points 6 & 10, and final outflow.

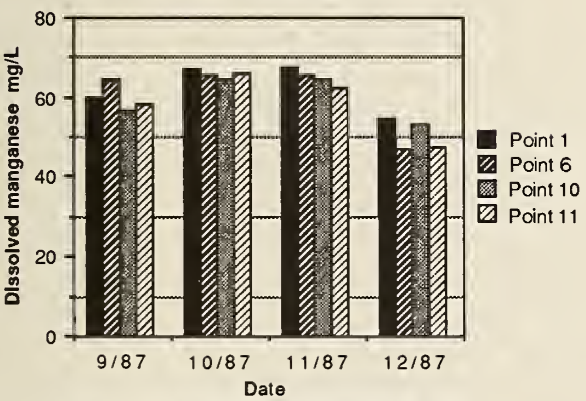


Figure 4.--Average dissolved manganese at AMD source, points 6 & 10, and final outflow.

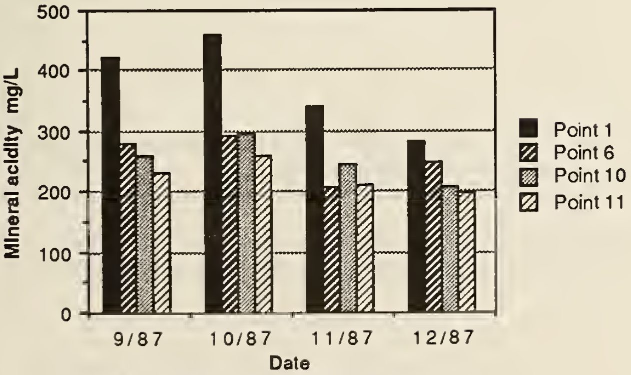


Figure 5.--Average mineral acidity at AMD source, points 6 & 10, and final outflow.

The WTS is significantly reducing the iron and acidity load of the AMD, but manganese values are not significantly reduced at this time. To date, the quantity of water entering and exiting the system has been equal. A small amount of seepage has been noted along the coal outcrop, upslope and immediately adjacent to the pond series ending with the *Typha* ponds (point 6), but the seepage is small enough that neither the quantity or quality of the flows in the WTS has been affected. The outcrop area has been planted in an attempt to control the seepage, since any drainage entering the WTS near its middle or end would obviously bias any results or conclusions regarding the effectiveness of the WTS.

Vegetation

The actual vegetative analyses will not begin until spring 1988 unless the algae ponds bloom during the winter months. The operational definition for "adsorbed minerals," in regard to the algae, is "that portion of the total minerals which can be extracted with the EDTA wash." The washing and filtration of the samples undoubtedly stresses the algae and may therefore bias the findings in relation to the concentration of adsorbed minerals. However, a similar study utilizing an EDTA wash to extract adsorbed zinc from algal samples indicated that the technique had no appreciable effect on the total concentration of surface-bound zinc, in that measurable intercellular zinc was not released by the technique (Bates, et al. 1982).

The most efficient method of mineral extraction for this study will be determined during the noted winter refinement period by testing varying lengths of extraction time, EDTA concentrations, and method of supernatant collection. The definition of adsorbed minerals will remain operational, however, since it will be impossible to unequivocally state that no intercellular minerals were released, and therefore measured, during the extraction process.

The ability to distinguish adsorbed from intracellular minerals will allow for a more complete understanding of the role of algae and the mechanisms of mineral accumulation in WTS's. Algal cell walls are composed of numerous, potential mineral adsorption sites as a result of their chemical makeup; however, these sites may or may not be active in transporting iron and manganese within the cell. The cell walls can act as both chemical and physical barriers in regulating mineral transport within the cell, thereby providing a means of metal tolerance to the algae by excluding potentially toxic ions from entering the cell (Foster 1977).

It is likely that the ashing data will show the majority of iron and manganese will be adsorbed versus intracellular; this is chiefly because of the known large concentrations of these minerals associated with the algae in the background ashings and the minerals' potential toxicity at these levels to the living cells.

Appropriate statistical analyses will be employed to determine whether intracellular concentrations of minerals are a function of the adsorbed concentrations, or if they are transported within the cell independently of the surface concentrations. Previous data also suggest that there may be an inverse relationship between iron and manganese accumulation in wetland vegetation (Kepler 1986), a relationship that will be tested in this study. The data will be further analyzed to determine if there is a correlation between total mineral concentrations in the AMD and total mineral uptake and accumulation in the algae; i.e., whether algae are more effective bioaccumulators at particular AMD mineral concentrations. Add to these findings the benefit of knowing the chemical form of the accumulated minerals, and predictions as to the success and long-term stability of WTS's will become more accurate.

SUMMARY

The removal of manganese in WTS's integrated with specific algae "ponds" may prove to be a successful treatment technique. Algae appear to be particularly well suited to this type of system in that they are widespread in AMD, are capable of accumulating relatively high concentrations of minerals, and are capable of rapid reproduction. The success of this single WTS and the mechanisms of the bioaccumulation of AMD minerals in algae will be determined in the proceeding months.

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TRACE METAL REMOVAL FROM STOCKPILE DRAINAGE BY PEAT[1]

Kim Lapakko and Paul Eger[2]

Abstract.--Batch reactor tests were conducted to determine the ability of peat to remove trace metals (Cu, Ni, Co, Zn) from one acidic and two near neutral mining stockpile drainages. In all three drainages, nickel contributed 70 to 85 percent of the trace metal concentration. The sum of the trace metal concentrations in the acidic drainage was 580 mg/L at pH 3.15. At a loading of 50 g dry peat/L, 60 percent of the trace metals were removed from this drainage after one hour of reaction, with no subsequent removal. The trace metal concentrations in the near neutral drainages totaled 1.2 mg/L at pH 7.4 and 9.2 mg/L at pH 7.9. Kinetic studies on these two drainages indicated that the majority of metal removal occurred in the first 20 hours of reaction and that equilibrium was approached after about 70 hours. At a loading of 5 g dry peat/L, metal removal of 80 to 90 percent was observed for solutions maintained at pH 7.4. Trace metal removal decreased as pH decreased from 7.4 to 4.0. Release of the bound metals to distilled water at pH 7.4 was slight, and was not greatly affected by elevated concentrations of calcium, magnesium, sodium, potassium and sulfate. Metal release increased as solution pH decreased and was greater yet when the peat was exposed to bog water. Column experiments were conducted on the near neutral drainage. Metal removal from the acidic drainage was 19 mg trace metal/g dry peat.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

[2] Kim Lapakko is Senior Engineer and Paul Eger is Principal Engineer, Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN.

INTRODUCTION

Five stockpiles containing low levels of metal sulfides are located at the LTV Steel Mining Company Dunka Site. Nickel concentrations in the drainages from these piles have ranged from less than 1 mg/L to nearly 40 mg/L. Concentrations of copper, cobalt, and zinc are also elevated. The Minnesota Pollution Control Agency (MPCA) recently concluded that metal concentrations in the creek draining the mine site were excessive, and in 1986 required that LTV examine means of reducing metal release from the watershed. The monthly average total concentration goals for in stream copper, nickel, cobalt and zinc were 0.030, 0.130, 0.010, and 0.047 mg/L, respectively. These values were based on United States Environmental Protection Agency (EPA) water quality criteria and other aquatic toxicity data (EPA 1980, 1984, 1986; MPCA 1988). The initial feasibility study indicated that wetland treatment may be a viable mitigation techniques for drainages with low or high trace metal concentrations.

In recent years interest has risen in the use of natural and constructed wetlands for treatment of acid mine drainage. Such applications are of particular interest in Minnesota, where peatlands cover an area of roughly 30,000 km^2. The focus of coal mine drainage treatment has been on increasing pH while reducing concentrations of acidity and iron. As mine drainage flows through wetlands, trace metals can also be removed from solution due to sequestration by peat, vegetative uptake, precipitation of metals with sulfide produced by sulfate reduction, and/or precipitation as metal hydroxides under conditions of elevated pH.

The occurrence of elevated trace metal concentrations in peat, under natural conditions, has long been recognized by geologists as an indicator of mineralization (Fraser 1961). As early as 1962 it was suggested that peat be used as a medium for removing metals from waste waters (Oreshko et al. 1962). Approximate geochemical enrichment factors (the ratio of the metal concentration in peat to its concentration in the solution with which the peat is in contact) for Cu, Ni, Co, and Zn have been reported as 2,400; 450; 6,900 and 8,600, respectively (Schnitzer and Khan 1972). Copper concentrations of 2.2 to 8.9 percent of the dry peat mass have been reported, as have nickel and zinc concentrations of 2.3 and 3.3 percent, respectively (Premi 1970, Smith et al. 1977, Szabo 1958).

The following conclusions were extracted from a literature review which addressed metal sequestration mechanisms and capacities of peat, as well as application of peat to waste water treatment (Lapakko et al. 1986). Ong and Swanson (1966) cited physical adsorption as the force which bound copper to peat. However, the majority of researchers concluded that the metal-peat bond is chemical in nature, specifying chemisorption, complexation, or chelation. It is not unlikely that both physical and chemical forces are involved in the reaction. Several researchers reported that ion exchange is involved in the reaction. To examine the sequestration of trace metals from mine drainage by peat, batch reactor and column studies were conducted. The laboratory results were compared to values observed in a white cedar swamp through which stockpile drainage flowed naturally (Eger et al. 1980).

METHODS

The peat used was a fibric, woody peat collected from the upper 0.75 m of an unimpacted black spruce bog in northeastern Minnesota. The pH of the peat was 4.5, as determined for a mixture of 15 cm^3 dry peat and 15 mL water, and the cation exchange capacity determined by the ammonium acetate method was 105 meq/100 g. Three drainages were examined, one of which was acidic (table 1). Drainage B was generated by a waste rock (0.057 pct Cu, 0.014 pct Ni) stockpile at the LTV Dunka site. The other two drainages were generated from small scale test stockpiles located near the Dunka site. The pile (FL1) generating Drainage A contained 0.35 pct Cu, 0.083 pct Ni, and 0.63 pct S. The pile (FL5) generating Drainage C contained 0.34 pct Cu, 0.084 pct Ni, and 1.41 pct S.

Erlenmeyer flasks (250 mL) covered with parafilm were used as batch reactors. A well-mixed condition was maintained by agitating the reactors on an Eberbach 6150 rotating shaker which was set at 125 excursions per minute. Kinetic experiments were conducted with 100-mL volumes of Drainages A, B, and C using peat loadings of 0.5, 1.0, and 50 g/L, respectively. Only one additional experiment was conducted with the acidic Drainage C. Metal removal was determined at seven peat loadings ranging from 0.5 to 50 g/L; solution pH was not controlled.

Experiments with Drainage A and Drainage B were more extensive. In batch reactor tests, metal removal at pH 7.4 was examined using peat loadings of 0.1 to 7 g/L. Three additional pH values, 4.0, 5.0, and 6.0, were also examined at three different mass loadings. pH was maintained by daily manual addition of NaOH or H_2SO_4 at concentrations of 1, 0.1, or 0.01 N, depending on the magnitude of adjustment required. Following the trace metal removal phase, release of metals from the solids was examined in a rinse phase with distilled water, a salt solution, and bog water. The distilled water rinse solutions were maintained at the same pH as the drainage solutions in the removal phase. The ions in the salt solution were Ca, Mg, Na, K and SO_4.

Table 1.--Composition of Drainages.

(Concentrations in mg/L unless otherwise noted.)

	Batch drainages			Column influent		Cedar swamp[1]
	A	B	C	A	B	
pH[2]	7.4	7.9	3.2	7.2-7.4[3]	7.2-7.9[3]	7.2
Cu	0.046	0.08	110	0.03	0.02	0.62
Ni	1.06	8.6	430	.86	5.4	18
Co	.029	.33	26	.05	.17	1.2
Zn	.10	.22	16	.11	.17	.38
CEU[4]	.19	1.3	180	.18	.75	3.7
Fe	NA	NA	NA	NA	NA	1.4
Mn	NA	NA	NA	NA	NA	6.5
Ca	510	300	390	270	230	280
Mg	62	142	520	26	130	220
Na	150	98	210	80	90	NA
K	50	10	34	30	8	NA
TAlk[5]	NA	NA	NA	18	51	110
TOC[6]	NA	NA	NA	10	16	22[7]

NA: not analyzed.

[1] Arithmetic mean value of stockpile drainage input over 14 months.

[2] In standard pH units

[3] Influent pH values varied over the course of the 2 to 4 month experiment.

[4] CEU = [Cu] + [Co] + 0.1 ([Ni] + [Zn]), with concentrations in mg/L.

[5] Total alkalinity as $CaCO_3$

[6] Total organic carbon as C

[7] Dissolved organic carbon.

Column experiments were conducted with these two drainages. A 2:1 mixture of wet peat to sand was required to maintain adequate flow rates in columns designed for a saturated flow rate of 5 bv/day (bed volumes per day, where one bed volume is the space occupied by the treatment bed, including voids). A saturated hydraulic conductivity of 5.4×10^{-4} cm/sec was determined for the peat-sand mixture at a dry bulk density of 1.2 g/cm^3. The peat-sand mixture in columns had a dry bulk density of 1.0 to 1.2 g/cm^3 and a porosity of 0.4 to 0.5.

Aqueous samples were filtered (0.45 micron) and analyzed for pH, sulfate, trace metals (Cu, Ni, Co, Zn), major cations (Ca, Mg, Na, K), and specific conductance. Solution pH and specific conductance were analyzed in the laboratory using an Orion 601A pH meter with a 9104 electrode and a Myron L conductivity meter, respectively. Serco Laboratories analyzed for sulfate using the barium sulfate turbidimetric technique. Metals were analyzed by atomic absorption in either the flame or flameless mode at the Minnesota Department of Natural Resources Minerals Division Office in Hibbing, MN.

RESULTS

To simplify presentation of results, the total trace metal concentration is occasionally presented in terms of "copper equivalent units" or CEU, which is calculated as:

$$CEU = [Cu] + [Co] + 0.1([Ni] + [Zn]) \quad (1)$$

This notion is based on data indicating that nickel and zinc are only one tenth as toxic as copper and cobalt (Lind et al. 1978).

A preliminary experiment was conducted to select mass loadings at which kinetic experiments would be conducted. This experiment indicated that as the peat loading increased, the solution pH decreased. For Drainage A and Drainage B the pH was reduced from 7.4 and 7.9, respectively, to about 3.7 at a peat loading of 50 g/L (dry weight). To limit the influence of peat on pH, and a potential resultant influence of pH on the kinetics of metal removal, loadings of 5 and 10 g/L were selected for Drainages A and B, respectively. The peat-induced reduction of Drainage C pH from an initial value of 3.22 was less than 0.3 units, and a loading of 50 g/L was chosen for the kinetic experiment with this drainage.

Solution pH was not controlled in the kinetic experiment, and in all cases it decreased over time. The initial pH of Drainage C was 3.1, dropping during storage from the value in the loading experiment. The pH decreased only slightly to 3.03 over 168 hours. For each trace metal, removal occurred within the first hour (fig. 1). With Drainages A and

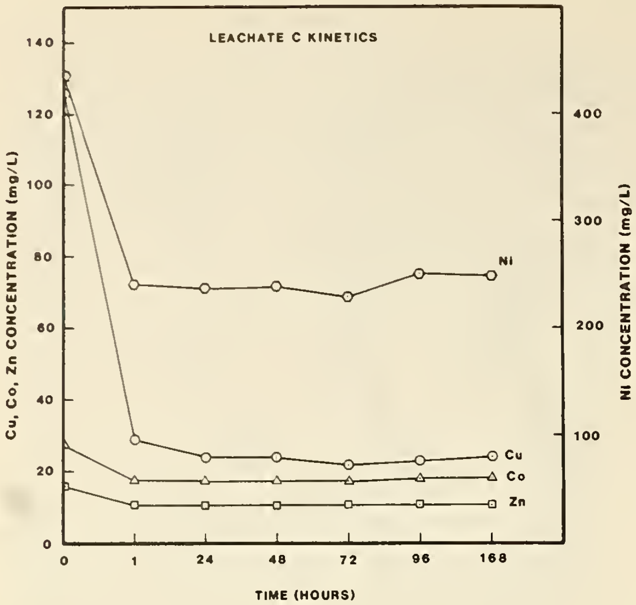

Figure 1.--Aqueous trace metal concentrations in Drainage C with a 50 g/L peat loading as a function of time.

B the pH was more affected and trace metal removal was less rapid. The pH decreased from 6.9 to 5.9 with Drainage A and from 7.7 to 6.1 with Drainage B. The majority of trace metal removal from these two drainages occurred within 24 hours and little removal occurred after 48 hours (fig. 2).

Isotherm experiments, in which the peat loading was varied, were conducted on each of the three drainages. Since the pH of Drainage C did not vary greatly with peat loading, data from the preliminary loading experiment were used. Peat loadings of 0.5, 1.0, 5.0, 10, and 50 g/L were used in this experiment. Equilibrium pH values fell from 3.22 for the untreated Drainage C down to 2.95 at a peat loading of 50 g/L. There was no detectable trace metal removal at peat loadings of 0.5 and 1.0 g/L and less than 20 percent removal at 10 g/L. At the maximum loading of 50 g/L, copper removal was about 80 percent while removal of nickel, cobalt, and zinc was all about 40 percent. Mass removal of nickel was the greatest of the metals, with concentrations reduced from 430 to 280 mg/L (fig. 3). No further experiments were conducted with Drainage C.

Experimentation with Drainages A and B was more extensive. To eliminate pH effects on isotherm experiments with these drainages, the pH in the reactors was maintained at 7.4 by regular addition of acid or base. With Drainage A, peat loadings of 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 g/L were used. Based on both percent and mass reduction, nickel removal was the greatest. From an initial value of 1.06 mg/L, nickel concentrations strictly

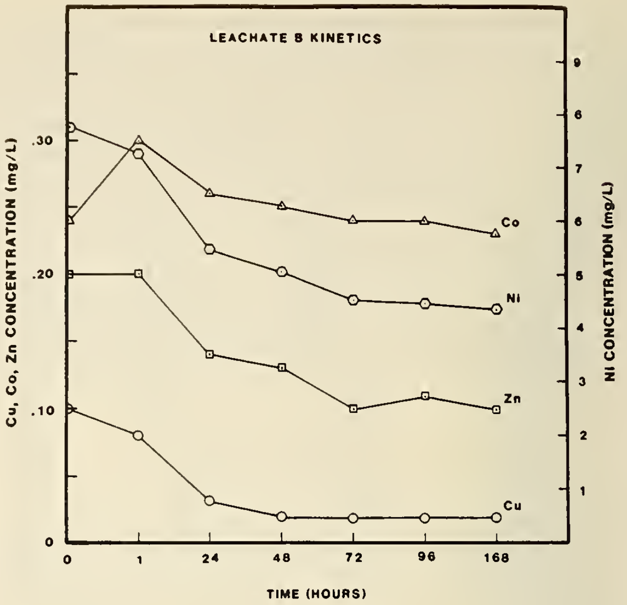

Figure 2. Aqueous trace metal concentrations in Drainage B with a 1 g/L peat loading as a function of time.

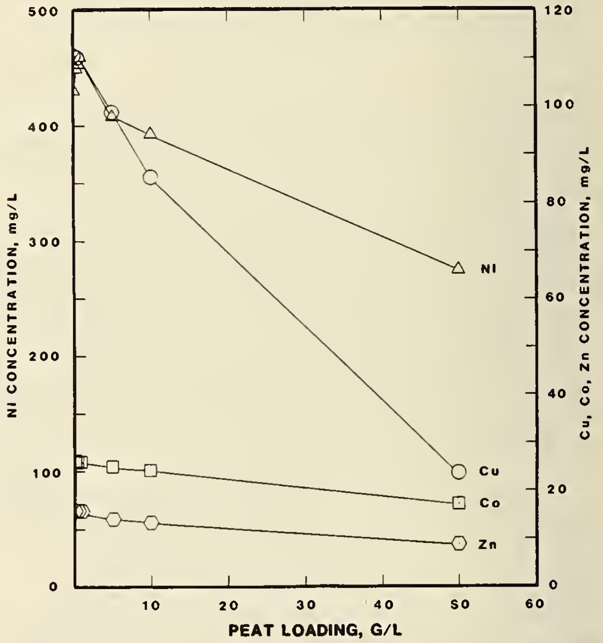

Figure 3.--Trace metal concentrations in Drainage C as a function of peat loading.

decreased to 0.78 and 0.09 as the peat loading increased from 0.1 to 5.0 g/L. The copper concentration of 0.046 mg/L was reduced to 0.013 mg/L at the 0.1 g/L loading and typically remained in the range of 0.007 to 0.009 mg/L over the remaining loadings. Cobalt and zinc concentrations were fairly constant with respect to

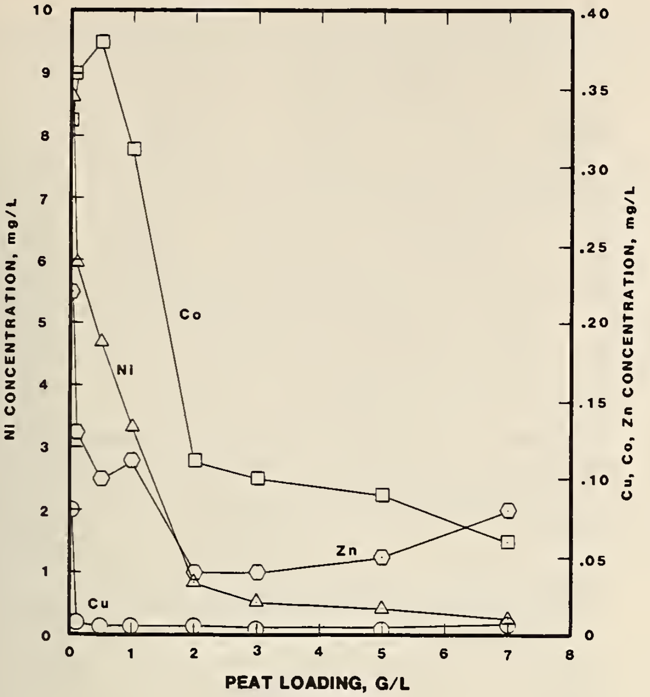

Figure 4.--Trace metal concentrations in Drainage B as a function of peat loading.

loading, with equilibrium values between 0.04 and 0.06 mg/L. There was an apparent release of cobalt to solution, but this was most likely attributable to an error in the analysis of the untreated drainage.

With Drainage B, peat loadings of 0.1, 0.5, 1, 2, 3, 5, and 7 g/L were used. From an initial value of 8.6 mg/L, nickel concentration decreased to 6.0 at the 0.1 g/L loading. Concentrations continued to decrease as loading increased and reached a minimum of 0.26 mg/L at the 7 g/L loading, a 97 percent concentration reduction. The reduction in copper concentration exceeded 90 percent at all loadings, with equilibrium concentrations in the range of 0.005 to 0.007 mg/L. The cobalt and zinc concentrations tended to decrease as the peat loading increased, with a maximum reduction of about 80 percent. The minimum observed aqueous concentrations of cobalt and zinc were 0.06 and 0.04 mg/L, respectively (fig. 4). Concentrations of calcium, magnesium, sodium, and potassium were also analyzed in this experiment. Calcium was the only one of these parameters for which removal was observed. Concentrations were reduced from 300 to 180 mg/L at the 70 g/L peat loading. Concentrations of magnesium and potassium were quite stable, typically remaining within ten percent of the initial values. Sodium concentrations increased only slightly, with an observed increase of 20 mg/L at the 7 g/L peat loading.

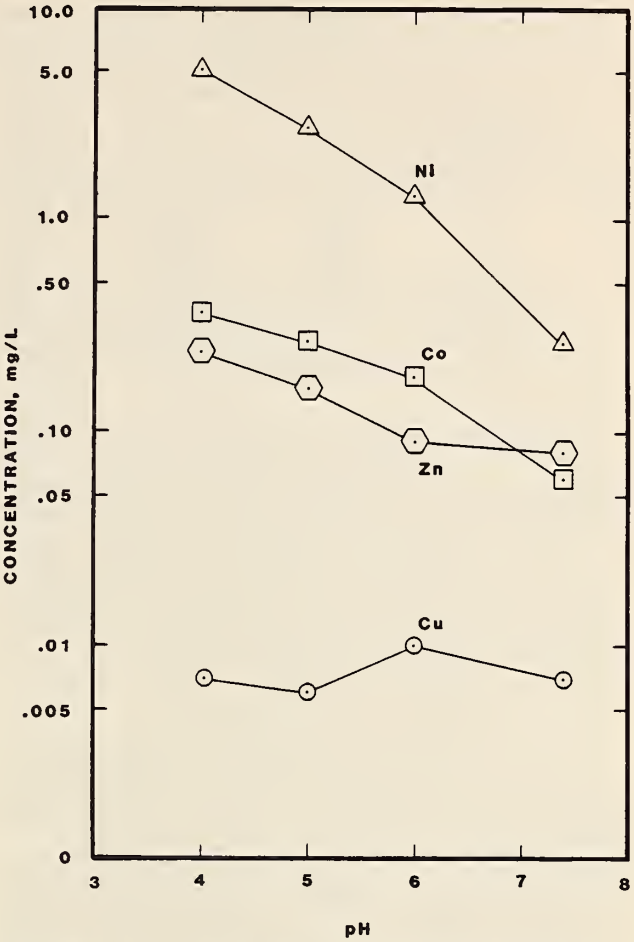

Figure 5.--Trace metal concentrations in Drainage B as a function of pH at a peat loading of 7 g/L.

The influence of pH on trace metal removal was examined in batch reactor experiments with Drainages A and B. With each drainage, three different peat loadings were exposed to drainage maintained at pH values of 4, 5, 6, and 7.4. In all cases trace metal removal decreased with decreasing pH (fig. 5). The results for equilibrium CEU levels were quantified as follows:

$$\log CEU_e = a\,(pH) + b \qquad (2)$$

The constants determined by linear regression are presented in table 2.

To determine how strongly the sorbed metals were bound, each of the solids used in the isotherm tests with Drainages A and B at pH 7.4 was placed in contact with 100 mL of distilled water and agitated as in the isotherm tests. The pH of the solution was maintained at 7.4 by regular addition of acid or base. Release from the solids to distilled water at pH 7.4 was small, typically less than five percent of the sorbed metal.

Table 2.-- Linear regression constants for log $CEU_e = a\ pH + b$[1].

Drainage A				Drainage B			
Peat Load (g/L)	a	b	r^2	Peat Load (g/L)	a	b	r^2
0.1	-0.038	-0.532	0.74	0.1	-0.047	0.38	0.64
1	- .13	- .127	.98	2	- .19	.66	.59
5	- .17	- .15	.95	7	- .28	1.11	.98

[1] CEU_e represents the equilibrium aqueous CEU concentration in mg/L.

Release tended to increase as the pH of the rinse solution decreased and as its ionic strength increased. For solids used with Drainage B, metal release at pH 4 was 2.5 to 5 times that at pH 7.4. Release to a salt solution at pH 7.4 was twice that observed for distilled water at the same pH. These trends were less pronounced for solids used with Drainage A. For both drainages, metal release to bog water at pH 4 was six to eight times the release to distilled water at the same pH.

Trace metal removal from Drainage A and B was also examined using a set of triplicate columns for each drainage. The results from each set of three columns were highly reproducible. The peat-sand mixture used in column tests with Drainage A depressed pH. Effluent values of 3.9 to 4.1 were observed, as compared to the influent pH of 7.4. With this drainage the peat-sand was replaced with a mixture of peat and low sulfur tailings (2 g wet peat: 1 g dry tailings) which produced a higher effluent pH and lower trace metal concentrations than the peat-sand mixture.

The columns containing the peat-tailings mixture reached breakthrough after 230 bed volumes (bv) of Drainage A flowed through the column at a rate of 5 bv/day. The maximum CEU reduction observed was 50 percent. The removal of individual metals tended to increase with the influent concentration (fig. 6). Removal was lowest for cobalt (essentially zero), and copper (6.3 mg/kg dry solid), and highest for nickel and zinc (85 and 11 mg/kg dry solid, respectively).

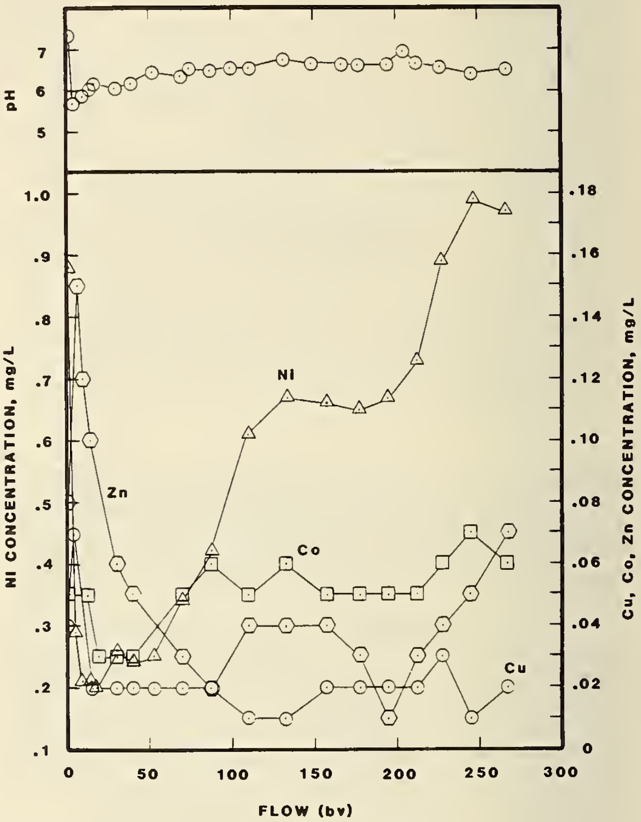

Figure 6.--Drainage A column effluent quality as a function of cumulative effluent volume.

Although the Drainage B columns did not reach total breakthrough (the point at which concentrations in the effluent equal those in the influent), the trends were similar to those observed for the Drainage A columns and in batch experiments. Metal removal was a function of trace metal concentration and increased as pH increased. The initial effluent had elevated trace metal concentrations, although less than influent levels, and depressed pH. The trace metal concentrations decreased fairly rapidly, reaching a minimum after about 25 to 35 bv of flow. Concurrent with this decrease was an increase in pH. Subsequently, the effluent CEU levels varied between 0.6 and 0.7 mg/L and pH stabilized at about 7. Some problems were encountered in maintaining flow rates, and were attributed to compaction of the peat-sand bed.

DISCUSSION

In a wetland setting, peat can provide a reasonably rapid removal of trace metals from mine drainage for an extended period. The removal kinetics are affected by drainage composition. To reach equilibrium, the peat-metal reaction required less than one hour with the acidic drainage and roughly 24 to 48 hours for the neutral drainages. The slower kinetics observed for Leachates A and B may have been influenced by several factors. First, the decreased peat loading and the lower metal concentrations would tend to slow apparent reaction rates, assuming typical relationships between rates and reactant concentrations. Secondly, dissolved organics which have leached from the peat may form soluble organometallic complexes and thereby effectively compete with functional groups on the peat for low concentrations of trace metals. Fulvic acid, for example, are present in peat and are, by definition, soluble in both acidic and basic solutions. Gamble et al. (1970) indicated that these ill-defined compounds can chelate copper. Thirdly, the influence of other cations, such as calcium, competing for binding sites on the peat would tend to be greater at low trace metal concentrations. Trace metals have a greater tendency than calcium to complex with organics. However, calcium might compete with some effectiveness since its concentration exceeded that of the trace metals by as much as four orders of magnitude. Even considering the slower rate, a retention time of 24 to 48 hours does not seem unreasonable for a wetland system treating mine drainage. A travel time of 50 days was reported for the flow of mine drainage through a cedar swamp in northeastern Minnesota (Eger et al. 1980).

The degree to which trace metal concentrations were reduced simulates the treatment efficiency in a field setting. The maximum metal removal from Drainages A and B, or treatment efficiency, typically was 60 to 97 percent of the aqueous metal. The fraction of nickel removed was greatest, while that of cobalt and zinc was the least. With Drainage C the copper removal was greatest (80 pct), while removal of Ni, Co, and Zn ranged from 35 to 40 percent.

Analyses of solution composition revealed the extent to which aqueous concentrations were reduced, but did not quantify the potential lifetime of peat in a field setting. One objective of the isotherm experiments was to generate data required for application of the Langmuir isotherm equation, and thereby determine removal capacities. With the exception of nickel, Langmuir isotherms did not describe the metal removal adequately. Similarly, Ryss and Hoffmann (1979) reported nonlinear Langmuir results for peat with Cu, Ni, Cd, and Zn. This was not totally surprising since this application of Langmurian theory assumes removal is the result of adsorption by a homogeneous surface from a simple solution. Both the peat and the drainages were complex in composition, and mechanisms other than adsorption were probably involved in removal reactions. At low concentrations, the complexation of trace metals by organics leached from the peat could have a significant influence on adsorption. The analytical error at the low concentrations, particularly for cobalt and zinc, is also greater. Since Langmurian theory did not describe the data, the theoretical removal capacities could not be calculated. Therefore, metal sequestration could be quantified only in terms of observed removal.

Wieder (1984) used the Langmuir equation to describe metal sorption onto peat, but his experimental approach differed in several aspects. First, he used a flow through system rather than batch reactors. Second, his solutions contained ferrous iron concentrations as high as 200 mg/L, as opposed to the relatively low trace metal concentrations typical of this study. Third, his solutions were prepared from ferrous ammonium sulfate, as opposed to more complex drainages used in these batch studies. Fourth, as opposed to the linear transformations used to calculate Langmuir constants in this study, he used a nonlinear technique, which appears to be superior (Rubin and Mercer 1981). More recently Wieder (1988) found that the nonlinear estimation method adequately determines the Langmuir adsorption capacity but yields questionable values for the energy of interaction for peat adsorption of metals from more complex solutions.

The mass of trace metals removed was influenced by aqueous metal concentrations and increased with increasing pH. The greatest mass removal was observed for nickel, which was the predominant trace metal in solution (table 3). Trace metal concentrations in Drainage B were higher than those in Drainage A. Similarly, trace metal removal from Drainage B, was greater than that from Drainage A. Although metal concentrations in Drainage C were higher than those in the other two drainages, the metal sequestration was not always higher. This was due in part to the pH of Drainage C, which was 4.2 units lower than that of the other drainages. The acidic conditions reduced the removal efficiency of the peat, as was verified in batch tests with Drainages A and B. This suggests that metal removal by peat in a wetland treatment system will be enhanced if the pH of acidic drainages is elevated prior to input to the wetland. Elevation of pH could also be accomplished by addition of alkaline solids to the peatland, but this could lead to chemical precipitation and possibly fouling of the peat. Ground water input to the peatland can provide some natural pH elevation.

Reduced removal at low pH was also observed in the column experiments. With Drainage A, tailings were required to neutralize the acid present on the peat. The alkalinity of Drainage B was three times that of Drainage A, and effectively neutralized the acidity of the peat. The initial effluent from both types of columns had relatively low reductions in trace concentrations and depressed pH. The pH

Table 3.--Metal binding by peat, values in mg/kg.

Metal	Batch Experiments[1]			Column[2]	Cedar swamp[3]
	Drainage A	Drainage B	Drainage C	Drainage B	
Cu	330	730	2,500	29	3,600
Ni	2,800	26,000	4,000	18,000	6,400
Co	2	110	300	580	3,600
Zn	200	900	200	890	270
Fe	NA	NA	NA	NA	26,000
Mn	NA	NA	NA	NA	15,000

NA: not analyzed.

[1] Maximum values observed based on reductions in aqueous concentrations.
[2] Average values for three columns; columns approached, but did not reach breakthrough. Drainage A columns excluded since it was difficult to discriminate between metal bound by peat and that bound by the tailings.
[3] Maximum observed total extractable metal concentration.

Table 4.--Geochemical enrichment factors in the laboratory and field.

Metal	Batch Experiments			Column	Cedar
	Drainage A	Drainage B	Drainage C	Drainage B	swamp
Cu	7,200	9,100	23	1,400	5,800
Ni	2,600	3,000	9.3	3,300	360
Co	69	330	12	3,400	3,000
Zn	2,000	4,100	12	5,200	270
Fe	NA	NA	NA	NA	19,000
Mn	NA	NA	NA	NA	2,300

NA: not analyzed.

depression was also observed in the batch experiments and was not surprising since the peat pH was 4.5. In addition to hydrogen ion equilibration between peat and water, hydrogen ions present in certain functional groups, for example carboxyl groups, would be released in ion exchange reactions involving cations in solution.

Geochemical enrichment factors (GEF, the ratio of the metal concentration in the peat to metal concentration in solution) normalized for differences in aqueous metal concentrations provided the closest simulation of field values. The GEF values calculated for the neutral drainages typically ranged between 1,400 and 7,200. The GEF values for copper and cobalt in a white cedar swamp receiving neutral mine drainage were in a similar range (table 4).

The nickel and cobalt GEF values observed in the field were lower than this range. This may be partly due to the fact that the values listed in table 4 tend to underestimate the actual GEF values. The tabulated values were calculated using the concentrations at the stockpile, which were higher than those at the site where the metal content of the peat was analyzed. Secondly, equilibrium with respect to these metals may not have been achieved in the swamp. Finally, the GEF value for zinc at the low aqueous concentrations observed in the field may tend to be aberrant. At these low concentrations there may be effective competition from aqueous phase complexing organics leached from the peat. Extremely low GEF values were also observed for cobalt in the batch tests with Drainages A and B.

Peat has been reported to sequester some trace metals preferentially over others (Bunzl et al. 1976, Ryss and Hoffmann 1979, Schmitzer and Khan 1972), and results of this study suggest that copper is preferred over nickel, cobalt and zinc. With Drainage C copper was preferentially removed, and copper concentrations in Drainages A and B were reduced to low equilibrium values at low peat loadings. The highest calculated GEF values were for copper, except in column experiments with Drainage B. In this experiment aqueous copper concentrations were very low, and the previously mentioned competition from aqueous phase organics may have been influential. Field data from other northeastern Minnesota sites indicate a preferential sequestration of copper by organics. Analysis of organic stream sediments contacting mine drainage yielded GEF values for copper, nickel, cobalt, and zinc of 25,000; 3,500; 8,300; and 3,800, respectively (Eger and Lapakko 1980).

The results of batch and column experiments indicate that solution compositional factors such as pH, metal concentration, and presence of competing metals influence trace metal removal. The composition and hydraulic conductivity of peat and wetland hydrology also influence trace metal removal. Consequently, the efficiency and capacity of peat to remove trace metals from specific drainages can be accurately assessed only on a site specific basis. Nonetheless, approximations can be used to gain some insight on the amount of metal removal a peatland can provide.

The batch and column experiments indicated that one kilogram of peat (dry weight) is capable of sequestering roughly 20 g of nickel from Drainage B, field data suggest a value of slightly more than 6 g. For this example a reasonable and convenient nickel removal capacity of 10 g/kg will be used. For field calculations removal capacity might be more appropriately expressed as 10 kilograms nickel per metric ton of peat. Assuming a peat depth of 1 m and a dry density of 0.1 tons/m^3, this implies a removal capacity of 10 tons of nickel per hectare of peatland.

In a natural peatland problems are presented by the low hydraulic conductivity of peat (Rycroft et al. 1975). Flow does not occur uniformly throughout the peat, but instead tends to occur over the surface and in the upper peat layer (Eger, et al. 1980). Consequently, it is advantageous to modify the peat layer in wetlands receiving mine drainages. Furrowing or disking the peat (perpendicular to the direction of flow) would allow the drainage to contact a greater surface area of peat and, thereby, improve metal removal. Flow through the lower layers of peat may also be enhanced by ditching perpendicular to the natural flow gradient. The effectiveness of this approach may, however, be limited by the slight gradients which are typical of natural peatlands. If peat were removed from the natural setting, the hydraulic conductivity could be increased by mixing the peat with inorganic solids, such as the sand or tailings used in the column experiments. Use of an alkaline material such as limestone, with this or other approaches, would further enhance trace metal removal by elevating pH.

Based on the desorption experiments with distilled water, the metals removed by the peat would remain tightly bound if the peat were contacted by precipitation. From 1983 through 1986 the volume weighted average precipitation pH at four sites in northeastern Minnesota ranged from 4.62 to 5.21, with a median of 4.82 (Twaroski, 1988). The degree of release would increase with decreasing pH. Indeed, it is possible that metals could be recovered from the peat when its capacity was reached. Metals could be released from the sorbed state by acidic solutions or by solutions containing strong complexing agents, as inferred by the elevated metal release to bog water. Exposing the metal loaded peat to high ionic strength solutions would also release bound metals. The batch experiments indicated that the acidic solution and bog water were superior for desorbing trace metals, but more efficient salt solutions than that used in these tests most likely exist. Another option would involve burning the spent peat, with possible attendant energy recovery, and recovering metals from the ash. The surface peat could be removed as its capacity was exhausted, thereby exposing the less taxed lower layers of peat.

SUMMARY

Laboratory studies indicate that peat is capable of reducing trace metal concentrations in mine drainage by more than 90 percent, and the reaction kinetics are adequate for peat to be a major trace metal sink in wetlands. The trace metal removal capacity is on the order of 20 g/kg, is dependent on trace metal concentrations, and decreases as pH decreases. At low concentrations, removal may be limited due to trace metal complexation by dissolved organics which leach from the peat. The batch and column data provided a reasonable simulation of trace metal removal in the field when the influence of solution composition was considered. If wetland systems are engineered to permit the contact of mine drainage with lower layers of peat, tens of tons of trace metals can be removed per hectare of peatland.

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NICKEL AND COPPER REMOVAL FROM MINE DRAINAGE BY A NATURAL WETLAND[1]

Paul Eger and Kim Lapakko[2]

Abstract.--Recently a considerable amount of attention has been focused on the use of wetlands, both natural and constructed, for the treatment of acid coal mine drainage. Wetlands also may have a significant capacity for removing trace metals from other types of mine drainage. Minnesota has many small and large peatlands near existing and potential mining developments, and the use of peatlands for the control of drainage quality is an attractive alternative to chemical treatment. A study has been conducted on a white cedar peatland receiving stockpile drainage which had an average concentration of 17.9 mg/L nickel and 0.62 mg/L copper. Surface and ground water, vegetation (white cedar (*Thuja occidentalis*), alder (*Alnus rugosa*), sedge (*Carex spp.*)) and peat were all analyzed for trace metal content. Based on mass balance calculations, and water quality data, essentially all of the copper and 80% of the nickel were removed by the peatland. Removal by peat accounted for greater than 90% of the overall metal reduction. Maximum observed concentrations in the peat were 6400 mg/kg nickel and 3600 mg/kg copper; while the maximum values for the vegetation were 239 mg/kg nickel and 10.1 mg/kg copper.

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INTRODUCTION

Wetlands, both natural and constructed, have been used successfully in the treatment of acid mine drainage (Kleinman, 1985; Wieder et al., 1982). Wetlands and the peat they contain have a significant trace metal adsorption capacity and offer a potential low maintenance treatment technique for metal laden mine drainage. In laboratory studies, peat has been used successfully to remove trace metals from various types of stockpile drainage (Lapakko and Eger, 1981, Lapakko et al., 1986).

Minnesota has 6 million acres of peatland most of which are located in the northern portion of the state. This area also has the highest mineral potential and exploration for gold and base metals is presently occurring on over 250,000 acres. Wetland treatment systems for mine drainage could be applicable to mining developments in Minnesota.

The objective of this study was to determine both the short-term and long-term effectiveness of a peatland in removing trace metals from stockpile drainage. This paper describes the initial phase of the study; the evaluation of the short-term effectiveness.

SITE DESCRIPTION

The initial phase of the study was conducted from July 1976 to August 1977 at the LTV Steel Mining Company's Dunka Mine in northeastern Minnesota. The Dunka Mine is a large open pit taconite operation, covering approximately 160 ha. The pit is 4 km long, .4 km wide and has a maximum depth of 110 meters. At this location, the Duluth complex, an igneous intrusion overlies the taconite ore and must be removed and stockpiled. The material has been separated based on copper content and has been stockpiled along the east side of the open pit. Drainage from all stockpiles and mine dewatering discharges (011, 012) flow to Unnamed Creek (fig. 1).

Drainage from a stockpile containing Duluth complex material with an average grade of 0.30% copper and 0.09% nickel flowed through a white cedar (Thuja occidentalis) peatland into Unnamed Creek (fig. 2). The stockpile covers 0.12 km^2; flow rates varied from zero during the winter to a maximum of 16 L/sec. Mean trace metal concentrations were 17.9 mg/L nickel, and 0.62 mg/L copper; the mean pH of the drainage was 7.2 (table 1).

The peatland covers 0.04 km^2, the depth of the peat ranges from 1.5 to 1.8 m, and the area is covered by 3-5 cm of standing water. The peat is generally well-decomposed, with decomposition increasing with depth, and is underlain by a layer of silty blue clay. Another white cedar

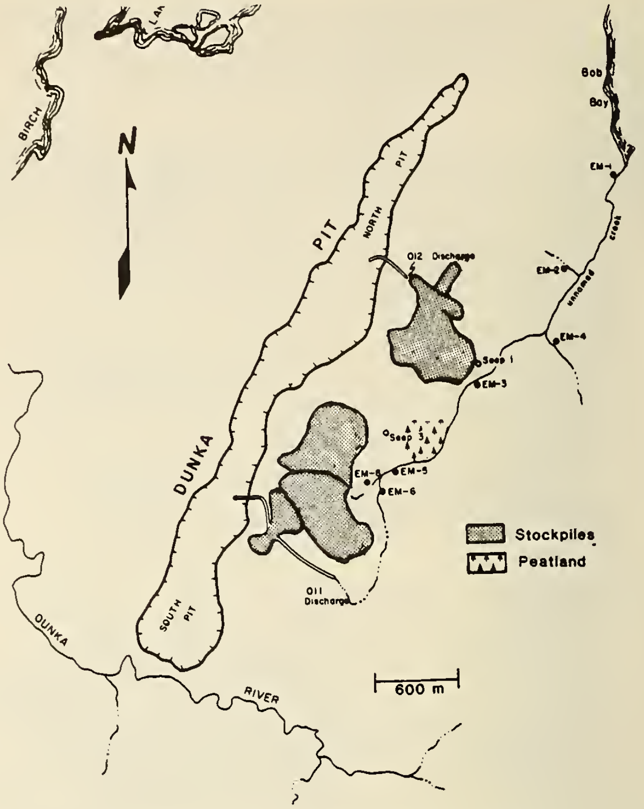
BIRCH
LAK
Bob
Bay
N
EM-1
PIT
NORTH
PIT
012 Discharge
EM-2
unnamed
creek
EM-4
Seep 1
EM-3
Seep 3
DUNKA
EM-8
EM-5
EM-6
Stockpiles
Peatland
011
Discharge
SOUTH
PIT
DUNKA
RIVER
600 m

Figure 1.--Dunka Mine, stockpile and sampling locations.

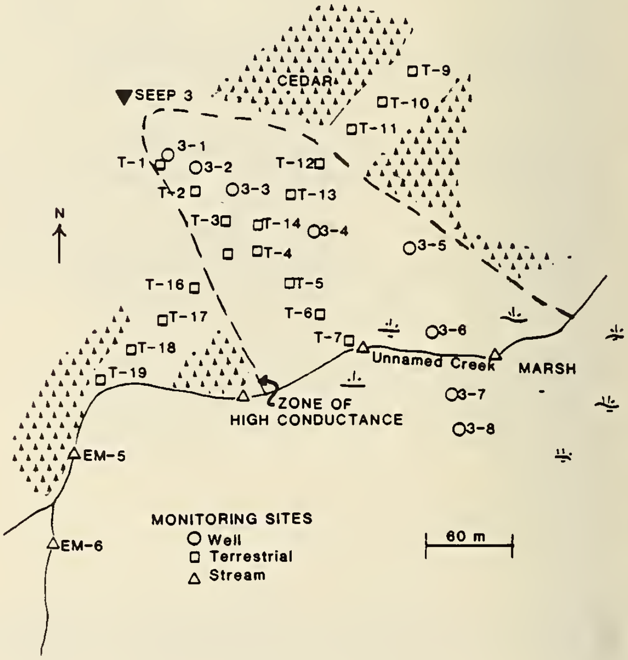
CEDAR
SEEP 3
T-9
T-10
T-11
3-1
T-1
3-2
T-12
T-2
3-3
T-13
N
T-3
T-14
3-4
3-5
T-4
T-16
T-5
T-17
T-6
T-7
3-6
T-18
T-19
Unnamed Creek
MARSH
ZONE OF
HIGH CONDUCTANCE
3-7
3-8
EM-5
MONITORING SITES
Well
Terrestrial
Stream
60 m
EM-6

Figure 2.—White cedar peatland.

Table 1.—Stockpile Drainage Water Quality, July 1976 through August 1977.

	Mean	Range	n
pH	7.2	6.68 - 7.79	24
Alkalinity (mg/l as $CaCO_3$)	113	47 - 206	24
Specific conductance (us/cm)	2540	890 - 3550	25
Calcium (mg/l)	285	93 - 388	17
Magnesium (mg/l)	225	52 - 288	12
Sulfate (mg/l)	1300	370 - 2600	17
Copper (mg/l)	.62	.04 - 1.7	24
Nickel (mg/l)	17.9	.4 - 39.8	24
Cobalt (mg/l)	1.16	.4 - 2.4	8
Zinc (mg/l)	.38	.07 - .65	12
Iron (mg/l)	1.44	.4 - 5.4	24

peatland in the same watershed but remote from trace metal sources, was selected as a control.

METHODS

Sampling stations were established at 6 sites along the stream, at each of the major stockpile flows (Em-8, Seep 1, Seep 3), at the two dewatering discharges (011, 012), and at 26 sites in the peatland (figs. 1, 2). Continuous flow data was collected at three sites along the stream (Em-1, Em-3, Em-5) at the largest volume of stockpile seepage (Em-8), and pumping records were available for the mine dewatering discharges. Flow measurements at all other stream and stockpile sites were collected every two weeks.

Water quality samples were collected at each site twice monthly during open water (typically April 1 - November 15) and approximately monthly during the winter. There was no drainage from any of the stockpiles during the winter.

In addition to the twice monthly samples special sampling programs were conducted to better quantify the source of metal input and the amount of metal transport in various parts of the watershed. Automatic samplers were used to collect composite samples along the stream, low flow samples were collected under the ice, and dye studies with Rhodamine WT were conducted to determine the travel times between the different sampling stations on the streams. Water quality samples were collected sequentially (from upstream to downstream) at the specific time intervals measured in the dye study so that the same parcel of water was sampled as it moved downstream.

In the peatland, at 8 of the sites (3-1 to 3-8) shallow wells and piezometers were installed. The shallow wells consisted of a perforated 10 cm diameter, 46 cm long PVC pipe, taped at the top to minimize surface water infiltration. The piezometers (1.5 m depth) were constructed of PVC, with a flange and a bentonite seal to prevent leakage. Specific conductance was sampled in the surface water at all 26 sites, and in the piezometers and wells. Specific conductivity surveys of the surface water were conducted monthly during the summer of 1977 to establish the path of stockpile seepage through the peatland. All 26 sites and additional sites perpendicular to the well line were sampled. In June and August, at sites 3-1 to 3-8, the water at the surface and in the wells and piezometers was filtered, and analyzed for trace metals by atomic absorption.

At the odd numbered T sites and at the control peatland within the same watershed, releves (Mueller-Dombois and Ellenberg, 1974) were used to describe the plant community; and visual estimates of plant damage were made. Samples of leaf tissue were collected at each T site for each of three species; white cedar (Thuja occidentalis), alder (Alnus rugosa), and Carex spp.. These samples were wet ashed using a $HNO_3/HClO_3$ digestion and analyzed for trace metal content using inductively coupled plasmaspectroscopy (ICP). Digestions and analyses were performed by Barringer Laboratories in Toronto, Canada.

At each site a composite of three peat samples was collected from the top 20 cm and analyzed for trace metals by total acid extraction (HF, HCl, HNO_3) (Meineke and Klaysmat, 1976). At four stations (3-1, 3-2, 3-5, 3-8) and the control site, trace metal concentrations were determined at approximately 25 cm depth intervals for the entire depth of the peat.

RESULTS

Stockpile drainage typically began in late March and ended around the middle of November, while mine dewatering and groundwater inputs maintained flow in the stream for the entire year. The mean nickel concentration at the mouth of the stream (site Em-1) was 0.1 mg/L and ranged from 0.03 to 0.22 mg/L. Concentrations throughout the stream exceeded the natural background levels (.001-.005 mg/L) for streams

Table 2.—Water Quality Summary at White Cedar Peatland, August 1977.

parameter	surface samples mean	surface samples range	shallow wells mean	shallow wells range	piezometers mean	piezometers range
specific conductance (us/cm)	3100	2250 - 3500	2600	2100 - 3000	270	213 - 325
copper (mg/l)	.13	.002 - .46	.001	.001 - .002	.001	.001 - .002
nickel (mg/l)	20	8.4 - 26.0	.6	.18 - .93	.03	.01 - .06

in the area, even during the winter when stockpile input ceased. Copper concentrations ranged from .001 to .006 mg/L and were similar to the values measured in unimpacted streams (.001-.005 mg/L) (Thingvold et al., 1979).

Water quality in the peatland varied with distance from the drainage input, depth in the peatland, and time. The specific conductance values in the surface water were used to define the path of stockpile drainage through the peatland. The boundary on the west side was particularly dramatic; specific conductance decreased from over 2000 to 400 within several meters. Specific conductance decreased as distance from the seep and depth in the peatland increased. Conductivity values decreased from 3000-3500 us/cm at the seep to 600-2000 us/cm near the stream with the majority of the reduction occurring over the final 200 meters (fig. 3). Specific conductance values were highest in the surface water and were an order of magnitude greater than those measured in the piezometers (table 2).

The reduction of copper and nickel concentrations with increasing distance from the seep in surface samples was greater than that of specific conductance (fig. 3). In both June and August the copper concentration was reduced by about two orders of magnitude. The greatest reduction occurred within the initial 100 meters of flow, with concentration remaining relatively constant, essentially at or slightly above background levels (⩽ .005 mg/l) over the final 200 meters. In June, nickel was reduced by about two thirds within the first 150 meters, but in August little reduction occurred in this portion of the peatland. In August, nickel did decrease by about two thirds over the final 200 meters of the peatland but the concentration near the stream (8.4 mg/L) was still about three orders of magnitude greater than background values. Surface concentrations of both metals were two to three orders of magnitude greater than the values from the wells and the piezometers (table 2).

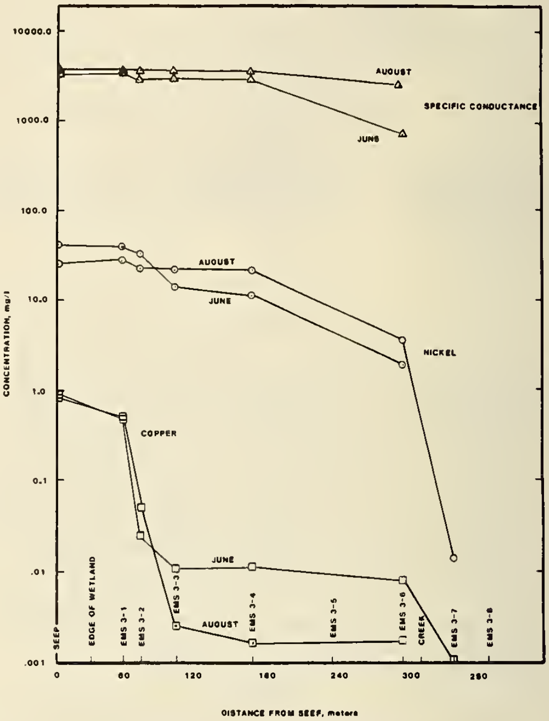

Figure 3.--Copper, nickel, and specific conductance in surface water in white cedar peatland, June and August, 1977.

Vegetation

The predominant vegetation in both the impacted and control peatlands was white cedar, alder and Carex. Damage levels were determined by the presence of chlorosis in the leaves, and gave only a qualitative indication of plant stress. High levels of damage to vegetation were observed at two of the ten T sites (T_1, T_{13}), but no definitive pattern relating damage to distance from the seep was observed.

Leaf tissue nickel concentrations were about one to two orders of magnitude higher in the impacted area than the values measured in the control peatland, where nickel was not detectable (⩽ 1 mg/kg). The highest nickel concentrations were generally found within the zone of high conductance water and the lowest values were measured outside this zone in the northeast section of the peatland at sites T_9-T_{11} (fig. 4). Elevated nickel values were, however, found at sites T_{16}-T_{19} which were outside the zone of high specific conductivity. Copper concentrations were about an order of magnitude lower than the nickel values even at sites near the seep, and there was no relationship between the

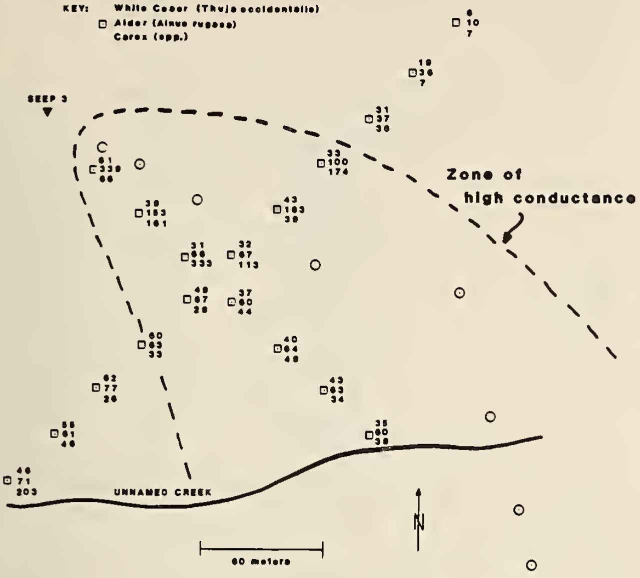

Figure 4.--Nickel concentration in vegetation, mg/kg (August 1977).

copper values and location in the peatland. Concentrations in the leaves of cedar and alder were slightly higher at the control than the values measured at the impacted area (table 3).

Peat

Nickel and copper concentrations in the peat decreased as distance from the seep and depth in the peat column increased. The maximum copper concentration of 3600 mg/kg was found in the top 20 cm sample near the seep (site 3-1). The concentration decreased with depth and the maximum value was about 6 times the value at the base of the peat (fig. 5). Samples collected at sites further from the seep had a more uniform concentration versus depth profile and concentrations near the creek were only 200-400 mg/kg. Surface nickel concentrations ranged from 6400 mg/kg near the seep to 1116 mg/kg near the creek and decreased with depth at all sites in the impacted area (fig. 6). Isopleths of the concentrations in the top 20 cm and the specific conductance in the surface water were used to define the area of drainage impact (fig. 7).

Generally the zone of high specific conductance corresponded to the area with the highest nickel concentrations in the peat. However, concentrations increased along the line from T_{16}-T_{19}, and the nickel values at T_{19} was comparable to the values within the zone of influence. Concentrations of the trace metals at the control peatland (25 mg/kg average copper, 65 mg/kg average nickel) and across the stream (site 3-8) were one to two orders of magnitude lower than the concentrations near the stockpile and were relatively constant with depth at both sites.

Mass Balance

To quantify the overall removal of copper and nickel occurring in the peatland a mass balance was calculated for the period of study. An overall watershed balance and a balance for the peatland alone were computed. Flow and concentration measurements were combined to compute overall mass inputs and outputs. Individual time periods were analyzed and error estimates for the nickel mass were made for Seep 3, Em-8 and Em-1. The overall mass values were estimated to be within ± 15% (Eger and Lapakko, 1980).

For the watershed, the major source of nickel and copper was the stockpile drainage, with seep 3 contributing about 87% of the total nickel input and 78% of the total copper input (table 4). The total input from stockpiles comprised 99.2% and 82% of the nickel and copper inputs, respectively. The total nickel input was 2087 kg and total output, as measured at the mouth of the stream (Em-1), was 340 kg. The overall nickel removal was 84%. Total copper input was 112 kg and the output was 9 kg, resulting in an overall copper removal of 92%.

The only significant input of nickel and

Table 3.—Trace Metal Concentrations in Vegetation.

	Peatland Receiving Stockpile Drainage (sites T1 - T19)				Control Peatland (mean, composite sample)		[1]Regional Values		
Plant Species	Copper (mg/kg) mean	range	Nickel mean	(mg/kg) range	Copper (mg/kg)	Nickel (mg/kg)	Copper (mg/kg)	Nickel (mg/kg)	No. of Sites
White Cedar (*Thuja occidentalis*)	2.6	2.1 - 3.8	37	8 - 62	4.1	1.0	No Data	No Data	1
Alder (*Alnus rugosa*)	7.8	4.8 - 10.1	82	10 - 239	12.1	1.0	3.9 - 12.1	1.0	3
Carex spp.	6.1	3.3 - 9.2	76	7 - 233	2.6	1.0	0.9 - 8.6	1.0 - 8.0	10

[1] Minnesota Regional Copper-Nickel Study

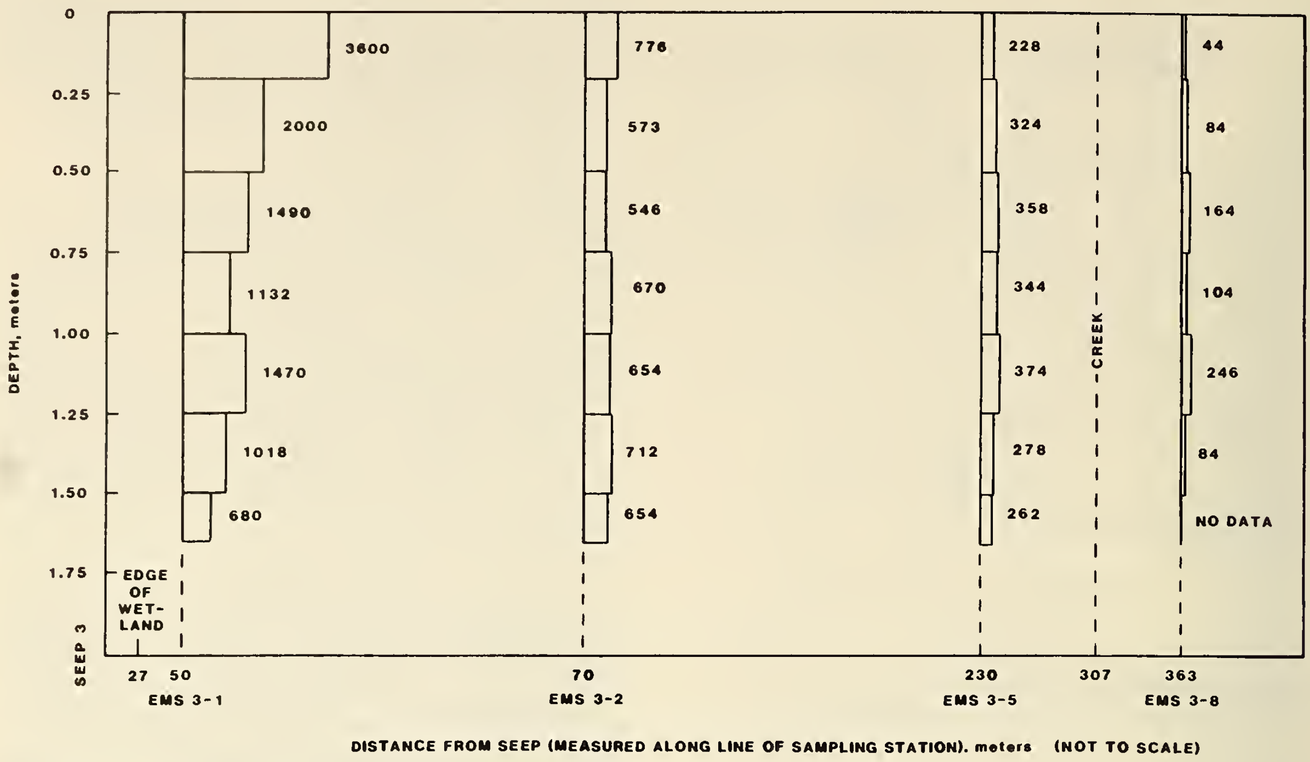

Figure 5.--Copper concentration (mg/kg) vs depth and distance from seep.

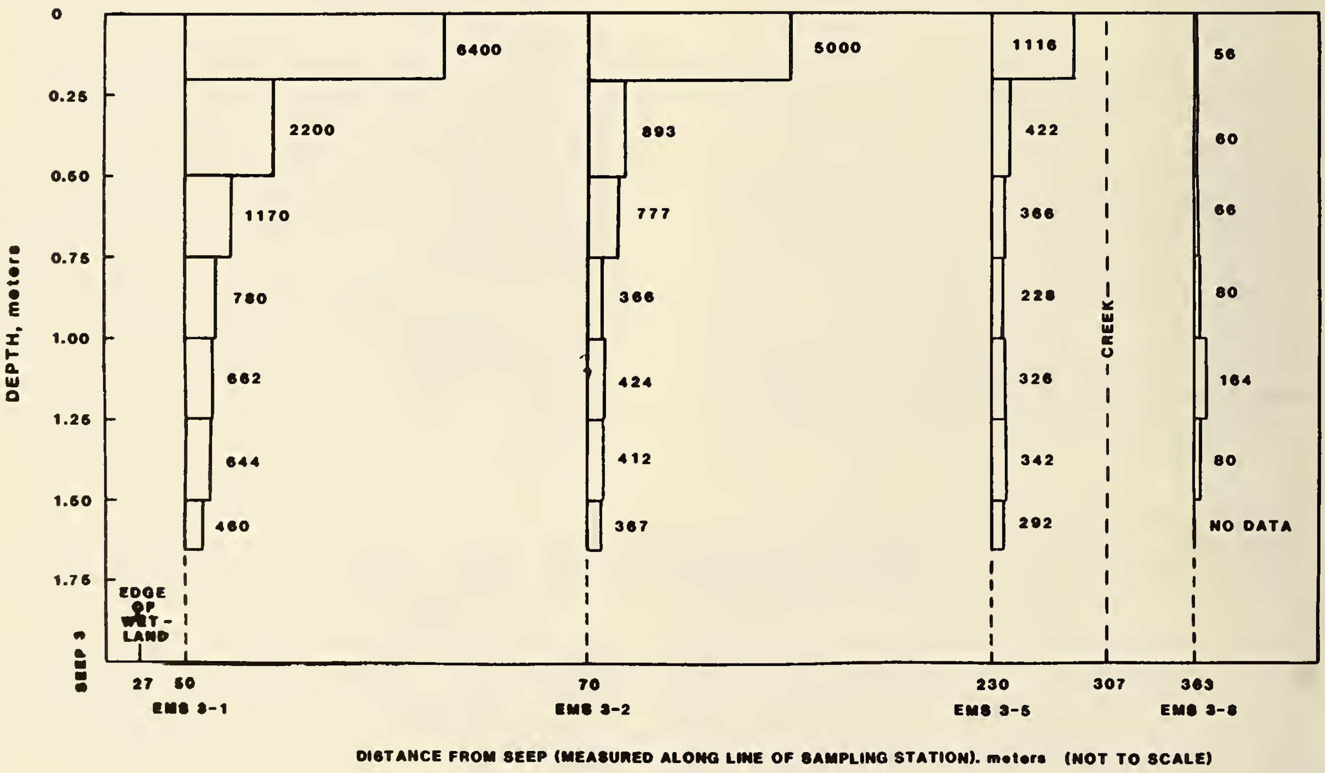

Figure 6.--Nickel concentration (mg/kg) vs depth and distance from seep.

Table 4.—Overall Mass Balance for Watershed.

	Volume (L X 10^6)	Mass (kg)		
		Nickel	Copper	Sulfate
Inputs				
Stockpile Seepage				
Seep 3	90	1810	72	103,000
Em8	184	150	4	128,000
Seep 1	29	110	16	72,000
Mine Dewatering Pumps				
011	2530	14	16	205,000
012	255	0.8	2	78,000
[2]Natural Runoff	426	2	2	13,000
Total Input	3514	2087	112	599,000
Outflow				
Em-1	3514	340	9	563,000
[1]Overall Removal		84	92	6

[1] $\frac{\text{input - output}}{\text{input}}$ X 100%

[2] Computed by difference.
Volume at Em-1 minus the sum of all input volumes.

Table 5.—Nickel Mass Input from Stockpile Drainage and Release from the Peatland to Stream.

Time Period	Nickel mass loading	
	Seep (mg/sec)	Input to Stream from Peatland (mg/sec)
7-15 to 10-25-76	45.4	3.6
12-07 to 12-10-76	0	1.2
5-05 to 5-13-77	1.1	5.4
8-16 to 8-17-77	111.0	28.0

copper to the white cedar peatland was the stockpile drainage from Seep 3. Nickel input during the 13 month study period was 1800 kg, and copper input was about 70 kg (table 4). The output from the peatland was much more difficult to quantify since there was no one single point where the drainage from the peatland entered the creek. The drainage occurred in a diffuse manner along the stream for about 250 meters (determined by specific conductivity measurements). The output of nickel was determined through the overall balance for the watershed, by comparing upstream and downstream nickel loads in the stream, and through low flow sampling along the stream (Eger and Lapakko, 1980). During the study period, discharge rates of nickel from Seep 3 ranged from 0 during the winter to 111 mg/sec, while contributions to the stream ranged from 1.2 to 28 mg/sec during the same period (table 5). The total estimated load from the peatland to the stream was about 300 kg, or about 80% of the nickel had been removed in the peatland. The copper output was not calculated since water quality data in the peatland and in the stream indicated that 1) copper concentrations were reduced to background levels within 200 meters from the seep and 2) there was no measurable input of copper from the peatland to the stream.

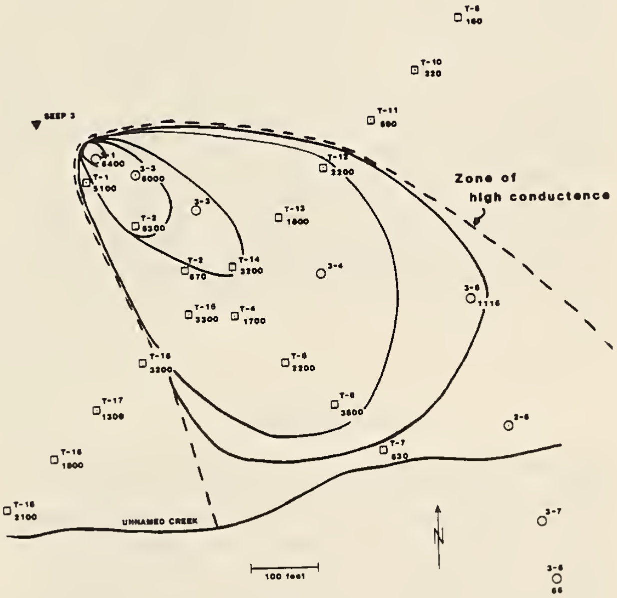

Figure 7.--Nickel concentration (mg/kg) in top 20 cm of peat, August 1977.

Metal accumulation was estimated in the water, vegetation and peat, using the specific conductance values to determine the boundary of the impacted area. Since the upper portion of the peat is about 90% water and since field observations indicated about 3-5 cm of standing water in the peatland, a substantial amount of metal could be stored in the water. Using the concentrations measured at the well sites and dividing the area between the sites, estimates were made for the mass of metal stored in the water. For nickel the total was 42 kg, with 76% of the metal being stored in the top 20 cm of the peatland.

Biomass estimates were made for cedar, carex, and alder (Ohman and Grigal, 1985; Dyer, 1967) and the average concentrations for each species was used to estimate the mass of nickel in each species. The total mass was less than 6 kg with cedar containing about 70% of the total.

The total mass of nickel contained in the top 20 cm of peat was calculated by using the area between the isopleths and applying the mean metal concentration to that volume of peat. Since a certain percentage of the metals were contained in the peat prior to the stockpile drainage a background correction was applied. The concentration at depths greater than 75 cm at the sites 3-2 and 3-5 was assumed to be representative of natural conditions. Estimates were made for the 20-75 cm depth based on the measured depth profiles and assuming that the isopleths at depth would be similar to those in the top 20 cm. Using these assumptions the nickel mass was estimated to be about 1150 kg in the top 20 cm and 350 kg between 20-75 cm. The mass of copper was calculated in a similar fashion and was estimated to be 77 kg.

DISCUSSION

Significant removal of nickel and copper has occurred in this watershed. The overall watershed balance indicated that about 1750 kg of nickel and 100 kg of copper were being removed. The largest source of metal input was Seep 3, but analyses of upstream and downstream loads in the stream revealed that only a portion of the nickel and none of the copper were transported through the peatland. Most of the metal removal in the watershed was occurring in the white cedar peatland.

Both the input - output calculations and accumulation estimates indicated that about 1500 kg of nickel and about 70 kg of copper were removed and stored in the peatland during the period of study. Based on the overall mass balance and water quality results, essentially 100% of the copper and about 80% of the nickel were removed. Analysis of the individual compartments demonstrated that greater than 90% of the metals were associated with the peat. Although the nickel and copper concentrations in the peat are on the order of several tenths of a percent, laboratory experiments with stockpile drainage have demonstrated that peat can accumulate up to 2% nickel during a continuous column removal experiment (Lapakko et al., 1986) and peat from the Tantramar Swamp in New Brunswick was found to contain as much as 10 percent copper (MacDonald et al., 1976). Typical metal concentrations for peat in Minnesota are about two orders of magnitude less than the values measured in the impacted peatland (Grigal and Nord, 1983). Metal values above background have been found near zones of mineralization, but were generally an order of magnitude less than the concentration in the study area (Meineke et al., 1977).

Specific conductance and peat metal concentrations indicate that the contact zone between the stockpile drainage and the peatland is confined to the upper portion of the peat, a zone referred to as the acrotelm, or the zone of active water movement (Romanov, 1968; Ingram, 1978). Since peat decomposition generally increases and hydraulic conductivity decreases with depth, only a small amount of the stockpile drainage will contact the lower levels of the peat and therefore treatment is restricted to the upper more permeable zone.

Even though the nickel values in the vegetation were elevated the removal of nickel by plant up take accounted for less than 1% of total nickel removal. Increasing the biomass in a wetland might provide greater metal removal, but for the metals in this study the increased removal would not appear to be significant.

CONCLUSIONS

Nickel and copper have been successfully removed from stockpile drainage as it flowed through a natural white cedar wetland. Essentially all of the copper and about 80% of the nickel was removed during the study period. Peat uptake accounted for over 90% of the removal while vegetation uptake provided less than 1% of the overall removal. Wetland treatment appears to offer a low maintenance alternative to seepage collection and treatment of metal contaminated drainage.

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EFFECTS OF A SPHAGNUM PEAT ON THE QUALITY OF A SYNTHETIC ACIDIC MINE DRAINAGE

Jonathan M. Dietz and Richard F. Unz

Artificial (constructed) wetland systems have attracted considerable attention in connection with the treatment of acidic mine waters. A study was undertaken to examine the effects of *Sphagnum* spp. and decomposed peat on pH, and iron and sulfate concentrations, in laboratory-scale reactors receiving synthetic mine water. Effluent was monitored for pH, iron, and sulfate. Depth profiles were examined for iron, sulfate, sulfide, pH, Eh, and sulfate-reducing bacteria. Addition of iron in the ferric state to the experimental units resulted in fluxing of highly visible oxidized iron which, according to profile and effluent data, underwent transformation to ferrous iron under reducing conditions. The addition of sulfate to the system correlated well with parameters of sulfate reduction, i.e., level of sulfate-reducing bacteria enriched in the peat, reducing Eh, sulfate loss, and concentrations of sulfide obtained. Under conditions of sulfate reduction significant decreases occurred in the effluent concentrations of total iron, soluble iron, ferrous and ferric iron, and sulfate following addition of sulfate to the synthetic mine water. Decreases in these chemical constituents were associated with the formation of iron sulfides important to the long-term retention of iron in the wetland environments.

INTRODUCTION

Acidic mine drainage, a waste product of both deep and surface coal mining, is formed when water and air contact sulfide-bearing minerals associated with the coal. Such disturbance of coal seams stimulates a series of chemical, and biochemical oxidation-reduction reactions mediated by iron- and sulfur-oxidizing bacteria, e.g., *Thiobacillus ferrooxidans* and *T. thiooxidans*. Acidic mine drainage characteristically contains high concentrations of metal ions, particularly iron species, and sulfate often at levels greater than 1000 mg/L. The mineral acidity of the waters vary, with pH values in the ranging from pH 2-3 up to pH 6.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society of Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988 Pittsburgh, PA.

[2] Jonathan M. Dietz is a Graduate Assistant and Richard F. Unz is a Professor of Environmental Microbiology, Environmental Pollution Control Program and Dept. of Civil Engineering, The Penn State University, University Park, PA.

Treatment of acidic mine drainage is required in order to meet water quality standards set by Federal and State regulations. Although costly and labor intensive, physical-chemical processes have been the usual methods of treatment. Lime, limestone, or sodium hydroxide are employed for neutralization of the acid waters followed by oxidation and precipitation of the metals. More recently, biologically based systems, including freshwater wetlands, have been investigated for application to the partial or full treatment of acidic mine waters (Unz and Dietz, 1986). Interest in wetlands for acidic mine water renovation has developed in response to the coal mining industry's need for a more economical method of treating acidic mine drainage. Cursory research on volunteer wetlands receiving acidic mine drainage has led to the belief that such environments may effect a decrease in the mineral constituents of the mine waters. These observations prompted laboratory and field investigations aimed at understanding the advantages and limitations of wetlands for acidic mine drainage treatment and the underlying mechanisms responsible. Gerber et al. (1984) studied Sphagnum moss placed in laboratory troughs and found the biomass capable of uptake and absorption of iron and manganese from synthetic mine water. Snyder and Aharrah (1984) examined a Typha community existing in a mine water region and observed considerable amounts of accumulated iron and manganese associated with the plants. Tarleton et al. (1984), based on results from constructed microcosms containing Sphagnum moss, proposed mechanisms of iron removal by wetland systems which included plant uptake, microbial oxidation and precipitation, absorption by organic deposits, and sulfide precipitation.

Rapid accumulation of incompletely decayed plant material in wetland communities results in extensive peat deposits and the formation of anaerobic conditions. Decomposition by obligate and facultative anaerobic bacteria may account for a large percentage of the reduction of organic material in a wetland system. In addition to pathways of intramolecular fermentation, organic carbon compounds may be anaerobically respired utilizing ferric iron and the sulfur of sulfate as final electron acceptors.

Relative to free ferrous iron, ferric iron is fairly insoluble in water becoming more so at higher pH values. In natural aqueous environments, ferric iron is precipitated as an insoluble oxide, oxyhydroxide, or jarosite. Tarleton et al. (1984) noted that iron oxides accumulated within their experimental units owing to the low solubility of oxidized iron. The stability of oxidized iron deposits in wetlands is not well understood. Oxides of iron are subject to microbial reduction when exposed to anaerobic conditions (Nealson, 1983). In addition, ferric iron may be reduced to ferrous iron by radical groups associated with humic materials and sulfides (Szilagyi, 1971 and Temple, 1964). The possibility exists that appreciable solubilization of the precipitated mineral deposits may occur in wetlands used to treat acid mine drainage.

Sulfate reduction occurs in nearly any environment where strong reducing conditions prevail. A well known sulfate-reducing environment is the salt marsh wetlands of coastal regions. The richly organic, anaerobic sediments and high concentrations of sulfate present in this environment provide for high rates of sulfide production mediated by sulfate-reducing bacteria. Although organically rich sediments exist in freshwater systems, production of sulfide is usually limited by the low concentrations of sulfate present. Smith and Klug (1981) demonstrated increased potential for sulfate reduction with increased supplements of sulfate in experiments with freshwater sediments. Tuttle et al. (1968) obtained evidence of sulfate-reducing bacteria in wood chip dams intercepting acidic mine drainage and Herlihy and Mills (1985) observed sulfate reduction in the sediments of a lake receiving acidic mine drainage. Results obtained by these workers indicate that sulfate reduction may ameliorate the characteristics of acidic mine drainage through increased pH and removal of dissolved iron in the form of iron sulfides. Tarleton et al. (1984) identified iron sulfides in their experimental microcosms, although, in small amounts compared to other iron fractions. The importance of sulfate reduction to the binding of metal ions in wetlands has not been resolved.

The present study was conducted to examine the impact of synthetic mine waters on laboratory microcosms, fashioned from transplanted wetland Sphagnum spp. and peat, with respect to (1) metal oxide transformations within the reducing zone of the peat and (2) potential for sulfate reduction in the peat with respect to increasing the pH and decreasing iron concentrations through formation of insoluble sulfide deposits.

MATERIALS AND METHODS

Experimental Units

Three rectangular chambers (30 cm x 40 cm x 20 cm) were constructed of plexiglass and fitted with inlet and outlet ports to provide a water depth of 12 cm.. A variable speed, multichannel, model 1203 Harvard peristaltic pump (Harvard Apparatus Co., Millis, MA) was used to deliver synthetic acidic mine water from a 55-L storage vessel to the units at a continuous flow rate of 2.8 mL/min. Tygon tubing was used in pumping connections between the feed reservoir and the units and silicon tubing (0.125 inch ID) was inserted in the peristaltic pump. The entire apparatus was located in an environmental room maintained at 20^{o}C and

Table 1. Composition of synthetic water applied to the microcosms during experimentation

	Influent Composition(mg/L)			
Component	Stabilization Water	Stage1	Stage2	Stage3
Fe(III)	0	30.0	0	0
Fe(II)	0	0	30.0	30.0
SO_4	0	0	0	100.0
Cl[1]	26.5	81.5	62.5	1.0
Ca	2.0	2.0	2.0	9.0
Mg	2.0	2.0	2.0	7.5
Na	5.0	5.0	5.0	5.0
K	6.0	6.0	6.0	6.0
NH_4-N	1.5	1.5	1.5	1.5
NO_3-N	0.5	0.5	0.5	0.5
PO_4-P	1.1	1.1	1.1	1.1
pH	3.5	3.5	3.5	3.5

[1] Chloride concentrations > reported value due to pH adjustment with HCl

60 percent RH. A cool white fluorescent light source providing approximately 120 ft-candles to the surface of microcosms was placed on a 12-hour on-off cycle.

Microcosms

Sphagnum spp. and underlying peat were obtained from the Bear Meadows area, a natural wetland in Central Pennsylvania. The Sphagnum biomass and the peat were removed successively and placed in plastic bags. The collected materials were transported to the laboratory and immediately placed in the experimental units which, subsequently, were filled with water from the collection area and allowed to stabilize under controlled conditions. During the stabilization period, which lasted approximately 4 weeks, water loss due to evaporation was replenished with distilled water. After the initial period of stabilization, a synthetic water, adjusted to a pH of 3.5 with HCl and containing mineral salts without iron and sulfate (table 1), was pumped into the microcosms. The microcosms were maintained on synthetic water for a 10-week period. Experimentation with the three microcosms was conducted in three successive stages (treatments) within the same experimental vessels. The chemical composition of the synthetic water used in each stage is given in table 1. Stage one units received synthetic water with oxidized iron (Fe III) in order to examine the effects of the peat on the stability of ferric iron and iron oxide deposits. Stage two and stage three units received synthetic water containing reduced iron (Fe II) and, in addition, stage three units received synthetic water which contained sulfate to determine the existence of sulfate reduction in the microcosms and its effects on the quality of the synthetic mine drainage. Effluent total, soluble (ferric plus ferrous), and ferrous iron, sulfate, and pH were measured every other day during treatment. Each stage was operated until the effluent parameters monitored remained stable for a period of 2 weeks. Depth profile analysis of the microcosms was made at the conclusion of an experimental run and included a determination of ferrous and total iron, sulfates, sulfide, pH, eH, and sulfate-reducing bacteria counts. Profiles of Eh and pH were measured in the microcosms at a distance of 1 cm from influent and effluent walls and at 10, 20, and 30 cm of the width and the values obtained from each depth averaged. Remaining profiles were determined for the effluent end of the tanks only with samples collected for each location from individual depths combined into one average sample. Between experimental stages, tanks were allowed to stabilize for a period of 3 weeks while receiving the initial synthetic feed water(table 1).

Analytical Procedures

Total and ferrous iron was determined using the phenanthroline method (APHA, 1975). Ferrous iron was determined directly. Total iron was determined after acidification of samples and reduction of ferric iron with hydroxylamine. Ferric iron was determined indirectly by subtracting ferrous iron from total iron. Sulfate analysis was performed turbidimetrically (APHA, 1975). Sulfide was analyzed by the methylene blue method (APHA, 1975). The pH and E_h values were measured with an Orion 399A pH/mV Analog Meter (Orion Research, Cambridge, MA) equipped with a Fisher Universal Glass pH electrode and a Fisher Platinum Indicating E_h Electrode (Fisher Scientific Co., Pittsburgh, PA). Sulfate-reducing bacteria were enumerated using a modification of the 5-tube MPN method described by Postgate (1984). Serially diluted samples were dispensed to 24-well Corning tissue culture plates (Fisher Scientific Co., Pittsburgh, PA) and incubated at 23°C in an anaerobic chamber under an atmosphere of N_2.

Data Analysis and Statistical Procedures

Effluent results of stage 2 and stage 3 units were statistically compared to evaluate the effects of sulfate reduction on iron and pH. Data collected during the last 2 weeks of stage two and stage three were averaged and statistically compared using a one-tailed ANOVA of comparison of means (Sokal and Rohlf, 1981).

RESULTS AND DISCUSSION

Ferric Iron Reduction

In the first stage of experimental work, microcosms, which had been purged of

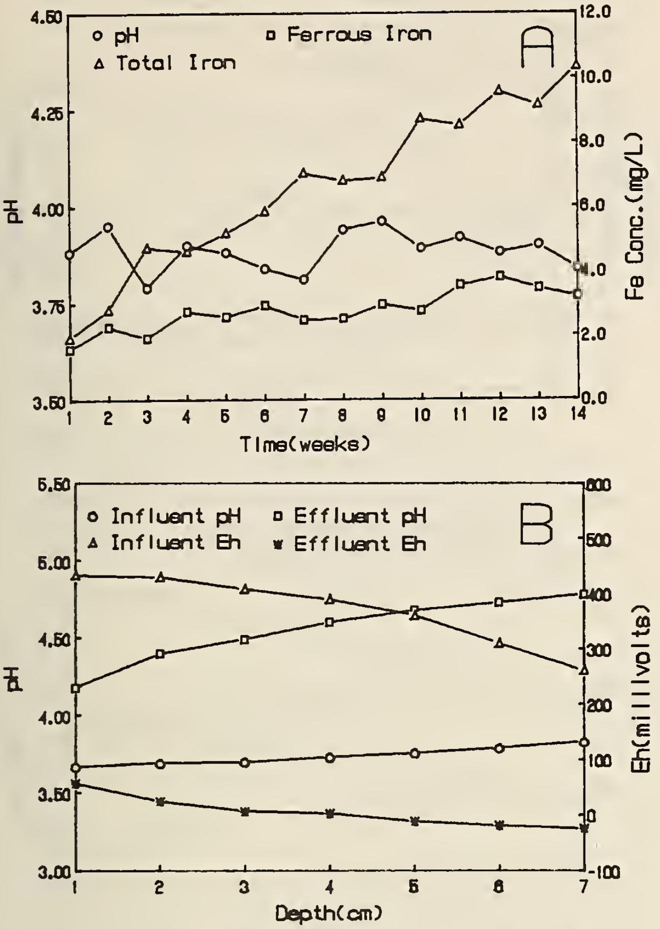

Fig.1. A.Effluent quality of stage one microcosms. B.Depth profile of influent and effluent pH and Eh parameters of stage one microcosms. Values are the mean of individual measurements on three microcosms.

all traces of ferrous iron, received synthetic water containing iron in the oxidized form. The charging of ferric iron(Fe(II)) to the experimental units resulted in the formation of highly visible iron oxide deposits in the peat. Subsequent appearance of ferrous iron in the effluent of the microcosms was considered evidence of internal reduction of ferric iron and the iron oxide deposits. The increased effluent iron levels, both total and Fe(II), over time (fig. 1A) may reflect the transformation of a greater proportion of the iron oxides deposited in the reducing zone. Depth profile data obtained at the end of the run are presented in fig. 1B. Both influent and effluent redox potential were markedly depressed with depth and were lower at the effluent region of the units. Stage one ferrous iron concentrations (fig. 5) increased slightly as E_h values diminished with depth. Interestingly, ferric iron reduction occurred at relatively high E_h values within the microcosms, suggesting that iron oxide deposits may be unstable towards solubilization and transformation within a major segment of the peat column.

Table 2. Depth profile counts of sulfate reducing bacteria of stage two and stage three.

	Sulfate-Reducing Bacteria(counts/mL)					
	Stage 2			Stage 3		
Tank	1	2	3	1	2	3
Depth (cm)						
2	5.6	36	360	68000	3600	6800
4	4.4	68	68	6800	4400	1100
7	880	3200	680	1800	28000	8800
10	56	5200	104	36000	25000	36

Sulfate Reduction

The potential for sulfate reduction in a low pH, freshwater environment was examined in stages two and three of the study. Microbial sulfate reduction in wetland environments at decidedly acid pH values is not considered to be a major activity and when such an event occurs there is usually the suspicion that the pH values represent bulk water measurements not reflective of the sediment microzonal pH (Tuttle et al., 1968). The results presented appear to support the premise of microbial sulfate-reducing activity at depressed pH values in the experimental microcosms. High numbers of sulfate-reducing bacteria (table 2) were found at all depths of microcosms studied, however, negligible influent sulfate concentrations (<0.5mg/L) in stage two of the study precluded significant sulfide formation. Nevertheless, high levels of sulfate-reducing bacteria existed in stage two units in spite of the absence of exogenous sulfate. The profile of the stage two microcosm (fig. 2B) reveals that reducing conditions were eventually established throughout the sediment even though sulfate was limited. In addition, significant reductions of effluent sulfate (as much as 10 mg SO_4^{-2}/L by comparison of influent and effluent [fig. 3A] values) were achieved by stage three microcosms. Depth profiles on stage three microcosms depicting measurements of sulfate and sulfide (fig. 4) and E_h (fig. 3) point to dissimilatory sulfate reduction as the principal process of sulfate removal. Decreasing sulfate concentrations with depth were observed in all three microcosms during stage three experiments. The possibility that the gradually diminished sulfate concentrations may have been due to diffusion limitations in the sediments rather than sulfate transformations was dispelled in consideration of the constant effluent sulfate concentrations, depth profiles of conservative ions, and the balance of sulfide produced against

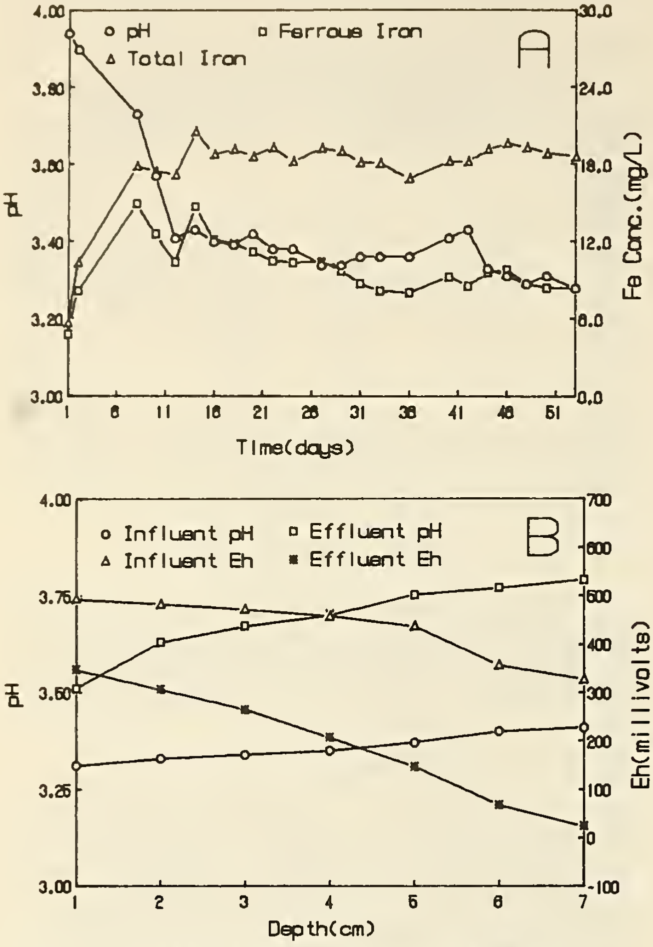

Fig.2. A.Effluent quality of stage two microcosms. B.Depth profile of influent and effluent pH and Eh parameters of stage two microcosms. Values are the mean of individual measurements on three microcosms.

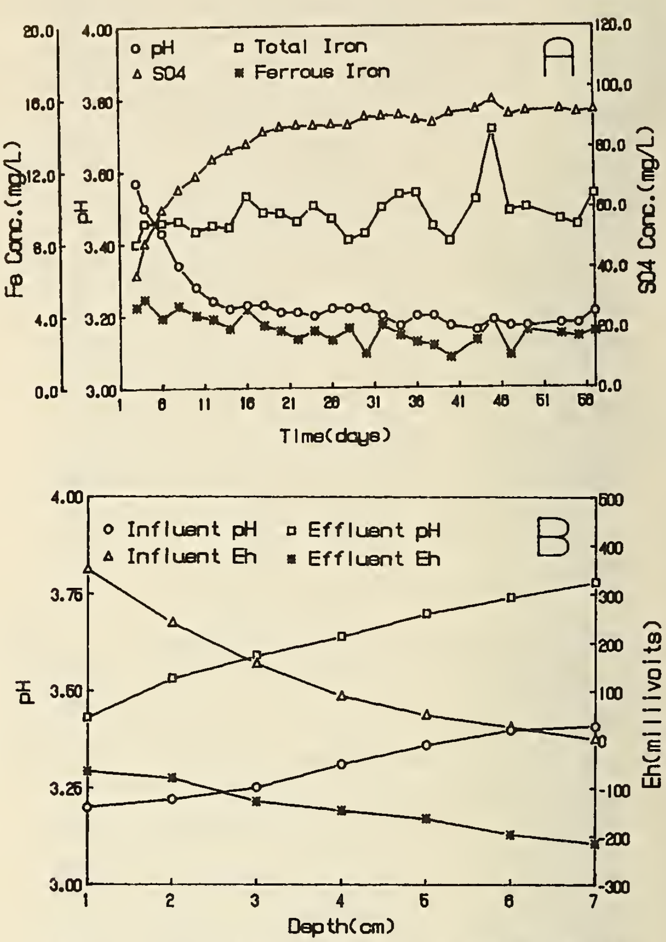

Fig.3. A.Effluent quality of stage three microcosms. B.Depth profile of influent and effluent pH and Eh parameters of stage three microcosms. Values are the mean of individual measurements on three microcosms.

sulfate lost. The large amounts of sulfide produced by stage three microcosms must have been derived from the sulfate charged to these units since no detectable sulfide was produced in sulfate-limited stage two units. Comparisons of E_h values(figs. 2B and 3B) in the microcosms during stages two and three revealed stage three E_h values were more characteristic of the reducing conditions expected where sulfate reduction would be occurring and in which sulfide would be present. The lower Eh values found in stage three units are likely to be as a result of the reduction of oxidized form of sulfate to sulfide.

Sediments displaying active sulfate reduction might be expected to effect an increase in pH owing to consumption of hydrogen ions by sulfide ions and to precipitate ferrous iron as FeS. The effect of sulfate reduction on effluent iron concentrations and pH was analyzed by statistically comparing the effluent results (figs. 2A and 3A) obtained with stage two (minor sulfate reduction) and stage three (major sulfate reduction) systems; both of which received a ferrous iron influent. The investigation found there to be significant decreases in all effluent iron concentrations from stage 2 to stage 3, but no significant increases in pH could be established.

Effluent iron concentrations (all forms) were lower by at least 50 percent in stage three units as compared to stage two units. High concentrations of effluent ferrous iron would be expected, as a result of increased reduction, in stage 3 experimental units as a result of low Eh (fig. 3B) values and high sulfide concentrations (fig. 4) present in the peat. Lower effluent ferrous iron concentrations actually resulted in stage three (fig. 3A) compared to the effluent of stage two (fig. 2A) presumably due to precipitation of the iron by sulfide. Although depth profiles of ferrous iron (fig. 5) in stage two and three are similar the appearance of visible black deposits in the peat of stage three microcosms was suggestive of iron sulfide precipitation. Acid digestion of the

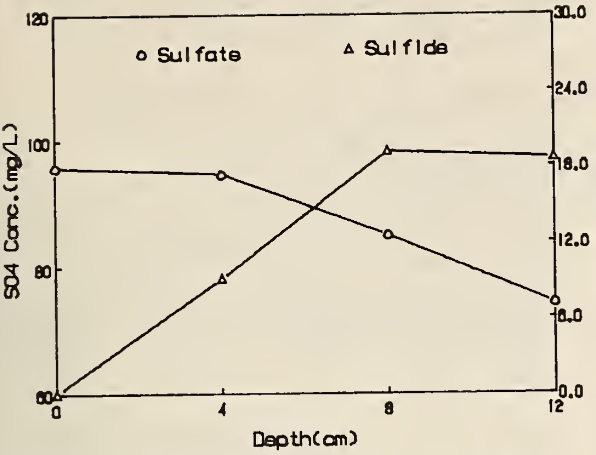

Fig.4. Depth profile of sulfate and sulfide in stage three microcosms at the conclusion of experimental run. Values are the mean of individual measurements on three microcosms.

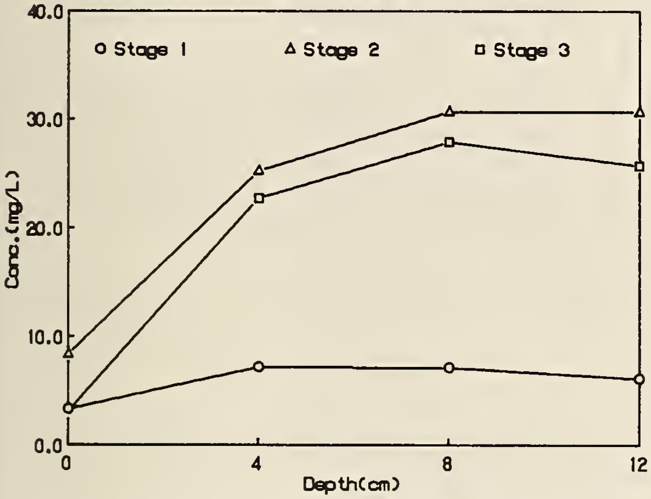

Fig.5. Depth profile of ferrous iron for all stages of experiment as determined at conclusion of experimental run. Values are the mean of individual measurements on three microcosms.

deposits followed by ferrous iron analysis indicated the presence of ferrous iron possibly as a result of the breakdown of iron sulfides. Although only ferrous iron was intended for delivery to stage two and three microcosms, in reality, an estimated 10 to 20% of the iron in the influent became oxidized during transport from the holding tank to the microcosms. The oxidized iron would be expected to become readily solubilized in the reducing sediments of the stage three microcosm, whereas, FeS precipitates presumably would remain intact.

As noted earlier, no significant difference between effluent pH values of stage two and stage three microcosms was found over time. Although sulfate reduction might be expected to produce lower hydrogen ion concentrations in the microcosms, this did not occur, presumably owing to preferential reaction of the sulfide ions with ferrous iron rather than hydrogen ions. Hence, only sulfide present in excess of that precipitated by iron may be available for hydrogen ion consumption. Examination of influent and effluent iron and sulfate concentrations of stage three units clearly demonstrated that sulfate losses did not exceed ferrous iron removal. In the present study, an excess of sulfide was never observed and the pH profile of the microcosm (stage three units) which exhibited sulfate reduction was not significantly different than that of stage two where only minor sulfate reduction took place. Although the pH was not increased as a result of sulfate reduction in this experiment, increased pH may still be a benefit of sulfate reduction. The design of this experiment may have prevented the occurrence of pH improvement due to low pH and high iron concentrations of the influent and the shallow depth of the tank. Further investigations are needed to determine whether sulfate reduction in a peat environment can improve the pH of acid mine water.

Table 3. Statistical comparison of stage 2 and stage 3 results. Averages of the three experimental units.

	Statistical Comparison		
	Averages(mg/L)		
	Stage2	Stage3	Probability
Total Fe	18.5	10.1	<0.001
Fe(II)	8.74	2.69	<0.001
pH	3.3	3.2	1
Sulfate		91.4	

1 Hypothesis rejected(Stage2 > Stage3)

CONCLUSIONS

The results of the laboratory study support the contention that ferric oxides deposited in Sphagnum microcosms are subject to microbial reduction and solubilization. Under these circumstances, the fate of iron oxide deposits in organically rich sediments must become a serious consideration in wetlands developed for acid mine drainage treatment.

Sulfate reduction was demonstrated at the low pH of the peat material of the experimental units with as much as 10% of influent sulfate concentrations being reduced. The sulfide produced through sulfate reduction had a significant effect on effluent iron concentrations in that more than 50% greater iron removal occurred in the sulfate-reducing microcosms as compared to sulfate-limited units. The iron removed was retained in the form of iron sulfides.

The important implications of the study for the development of wetlands earmarked for acidic mine drainage treatment lie with peat-producing plants, such as Sphagnum, Typha, Carex, and

Scirpus. An artificially constructed system, in which the reducing zone is sufficient to solubilize and reduce oxidized iron species, but lacks the presence of sulfide for precipitation of the iron, may eventually release soluble iron at levels in equilibrium with that of the influent. Construction of deep cells for the collection of fermentable plant matter should assure adequate reducing potential for microbial sulfate reduction in the wetland bed since acidic mine waters normally contain high sulfate concentration environment.

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IRON AND MANGANESE REMOVAL IN A TYPHA-DOMINATED WETLAND DURING TEN MONTHS FOLLOWING ITS CONSTRUCTION[1]

Lisa L. Stillings, Jeffrey J. Gryta, Tedd A. Ronning[2]

Abstract. A *Typha*-dominated wetland was constructed in September 1986 to remove iron and manganese from a surface mine seep characterized by an average flow of 10 gpm, pH of 5.5, and maximum concentrations of 40, 50, and 2700 ppm Fe, Mn, and SO_4^{2-}, respectively. *Typha* were planted at 1-ft centers in a 110 by 20 ft basin containing a basal 6-inch layer of agricultural-grade limestone and an upper 10-inch layer of an equally proportioned mixture of peat, compost, and sandy soil. Surface waterflow volume was recorded with inlet and outlet weirs, and rainfall was measured by a continuous recording rain gauge. Water samples were collected at the inlet and outlet of the wetland, and at 33 surface locations within the basin. Substrate interstitial water was sampled from six, two-level piezometer nests. All samples were analyzed for Ca, Fe, K, Mg, Na, Mn, P, and SO_4^{2-}, on a biweekly basis from October 1986 to July 1987. Seventy-four percent of the 186 kg of iron introduced to the system was removed during this period. Manganese removal was less successful; only 8% of the 368 kg influx was removed. Periods of increased waterflows corresponded with the smallest percent reduction of influent mass concentrations. The greatest reduction of influent mass occurred during the June 1 sample period, when 26.4 kg of iron, and 14.2 kg of manganese, were removed from solution. The wetland's ability to remove iron and manganese varied with time and location within the basin. Inlet flow volume, basin length, and water flow through the substrate were important factors affecting the retention of influent iron and manganese.

INTRODUCTION

Wetlands have been used since the 1970's for the treatment of acid mine drainage (AMD) and municipal wastes. Studies conducted by Huntsman et al. (1978) and Wieder and Lang (1982) have compared influent and effluent concentrations of AMD passing through wetlands. Wieder et al. (1985) and Girts and Kleinmann (1986) have examined the wetland flow conditions which surround AMD amelioration. Recommendations regarding the most effective flow rates, basin size, and vegetation types have

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been made by Kleinmann et al. (1986) Girts and Kleinmann (1986) and Girts et al. (1987). Research has also been conducted with wetlands for the treatment of municipal waste (Wile et al. 1985, Kadlec 1987), and while AMD and municipal waste influent possess inherently different qualities, criteria such as length and retention time are found to be important in the successful treatment of these two types of contamination. Detail is lacking, however, pertaining to where metal removal takes place within wetlands, what chemical conditions surround removal, and how removal rates vary with time. In this study, an instrumented wetland was constructed to quantify iron and manganese removal over a 10-month period following wetland construction. The wetland received flow from an AMD seep emerging from spoil reclaimed following mining of the Middle Kittanning (#6) and Lower Kittanning (#5) Coals of the Allegheny Formation in Tuscarawas County, OH.

METHODS

Wetland Construction and Instrumentation

Based upon an average flow estimate of 10 gpm, a 110 by 20 ft basin was constructed (fig. 1) following the recommended size of 200 ft^2. of wetland/1 gpm of flow (Kleinmann et al. 1986). The basin was leveled and filled with six inches of agricultural-grade limestone which, in turn, was covered with a 10-inch humic layer consisting of an equally proportioned mixture of peat, compost, and sandy soil. The limestone was placed as a distinct layer and not mixed with the humic soil to avoid coating the limestone with a ferric hydroxide precipitate (Kleinmann et al., 1986). Cattails (Typha) were collected from the surrounding area and planted in the basin at 1-ft centers. Cores taken one month later showed that these layers had compacted to approximately 5.5 inches of limestone, and 7 inches of humic material.

The water budget is recognized as a key factor affecting water quality and wetland functions (Kadlec 1987). Therefore, 40^o V-notch weirs with continuous water level recorders were installed at the inlet and outlet to measure surface waterflow into and from the wetland. Flow volumes were calculated from the following equation for sharp-edged, V-shaped weirs (Brakersiek et al. 1979):

$$Q = C \times 8/15 \times \sqrt{2g} \times \tan(\theta/2) \times H^{2.5} \quad (1)$$

where,

Q = discharge (ft^3/sec)

C = weir coefficient (0.582 for a 40^o V-notch weir)

θ = total angle of notch (degrees)

H = head above the lowest point of the notch (ft), and

g = gravitational acceleration (32.17 ft^2/sec).

A weighing-bucket continuous recording rain gauge was placed at the site to measure rainfall; potential evapotranspiration was estimated from evaporation pan data collected during the spring/summer months. Additionally, six, two-level piezometer nests were placed within the basin: the lower level sampled subsurface water within the bottom 3 inches of the humic substrate, and the upper level sampled the top 3 inches of the substrate.

Sampling Procedure and Chemical Analysis

Wetland water samples were collected on a biweekly basis from October 11, 1986 through July 3, 1987 from the piezometers, the inlet and outlet weir pools, and from 33 surface sites defined by an 11-column by 3-row sample grid (fig. 1). Nineteen separate collections were made. Frozen wetland surface conditions, and site inaccessibility due to excessive rainfall precluded the collection of some samples. Chemical analysis included Ca, Fe, K, Mg, Na, Mn, SO_4^{2-} and orthophosphorus. Inductively Coupled Plasma (ICP) spectrometry was used for all analyses except for SO_4^{2-} and ortho-P. These were determined by colorimetric procedures outlined by Hach (1986), with one modification: rather than reading sample concentration directly from the spectrophotometer, a series of standards was analyzed with each sample batch to establish a regression relation of concentration versus absorbance. Sample concentrations were then determined with this equation.

Water Budget Analysis

Water budget volumes were calculated as described in LaBaugh and Winter, 1984, by dividing the study period into intervals whose midpoints correspond to the date of water sampling. Budget components include inlet flow (If), outlet flow (Of), rainfall (Ppt), potential evapotranspiration (Pet), and change in volume of surface water stored (ΔS) within the basin (volume determined by multiplying wetland area times average surface water depth). All of the above components were calculated for each interval, and the following equation was used to determine the residual (Res) component:

$$If + Ppt - Of - Pet - \Delta S = Res \quad (2)$$

A positive residual value denotes a net water gain or an ungauged loss of water (such as vertical seepage down through the basin), while a negative residual value denotes a net water loss or an ungauged source of water (such as vertical seepage up into the basin). Residual values might also reflect operator and/or instrument error.

Mass Budget Analysis

Following water budget analysis, a

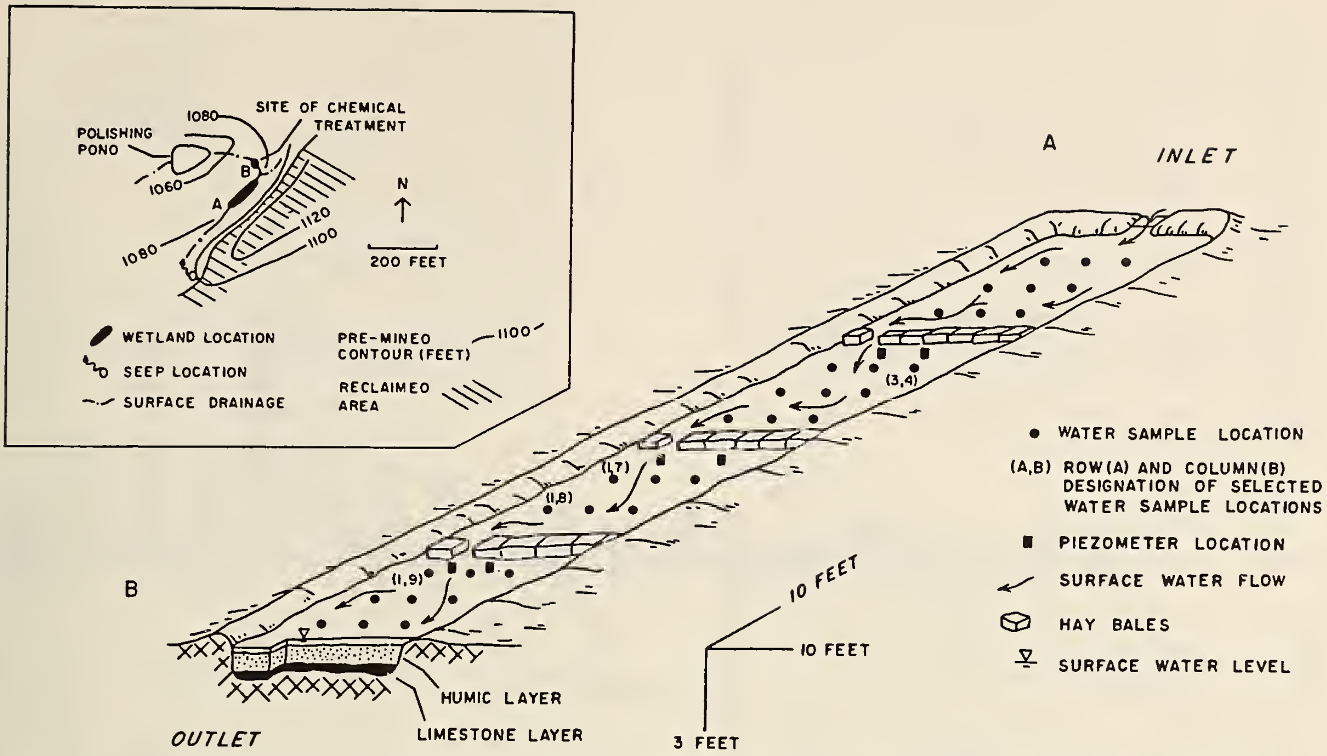
POLISHING POND
1080
SITE OF CHEMICAL TREATMENT
1060
B
A
1120
1100
1080
N
200 FEET
WETLAND LOCATION
SEEP LOCATION
SURFACE DRAINAGE
PRE-MINED CONTOUR (FEET)
1100
RECLAIMED AREA
A
INLET
(3,4)
(1,7)
(1,8)
(1,9)
B
OUTLET
HUMIC LAYER
LIMESTONE LAYER
10 FEET
10 FEET
3 FEET
WATER SAMPLE LOCATION
(A,B) ROW(A) AND COLUMN(B) DESIGNATION OF SELECTED WATER SAMPLE LOCATIONS
PIEZOMETER LOCATION
SURFACE WATER FLOW
HAY BALES
SURFACE WATER LEVEL

Figure 1.--Schematic drawing of the wetland basin with sample locations. The insert locates the wetland with respect to the AMD seep and the site of pre-wetland chemical treatment.

total mass flux for each interval was calculated by multiplying inlet and outlet flow volumes by their respective inlet and outlet concentrations. Assuming that negative residual volumes (equation 2) resulted from an ungauged source, these were multiplied by the inlet concentrations and added to the amount of mass entering the wetland. Positive residuals were attributed to ungauged outflows, and these were multiplied by the outlet mass concentrations and added to the amount leaving the wetland. Total influx was calculated as the sum of the influx values for each interval. Total outflux was determined in a similar manner. Inflow and outflow were the only water budget components used in mass budget calculations because iron and manganese concentrations in rainfall were assumed to be negligible, and because change in surface storage accounted for less than one percent of the total water budget.

RESULTS & DISCUSSION

Concentrations of Fe, Mn, and SO_4^{2-} at the seep varied throughout the study period, and while their maximum concentrations were 44, 50, and 2720 ppm, respectively, they averaged 31 ppm Fe, 34 ppm Mn, and 1130 ppm SO_4^{2-}. Mass concentrations at the inlet to the wetland averaged 13 ppm Fe, 30 ppm Mn, and 990 ppm SO_4^{2-}; evidently Fe and SO_4^{2-} were removed from solution while the water flowed through a ditch leading from the seep to the wetland (insert, fig. 1). The following discussion considers only the mass concentrations which actually entered the wetland.

Overall, 74% of the 186.4 kg of iron delivered to the wetland during the study period remained within the basin. Each sample interval within this period consistently displayed a smaller mass outflux than the influx, indicating that iron removal continued through time (fig. 2a). The smallest percentage of iron removal, 43%, occurred on two separate occasions: first, during the December 8 interval, when 2.4 kg of iron were removed from the flow; and second, during the April 15 period, when 6.2 kg were removed (fig. 2a). The largest reduction occurred over the June 1 sample interval, with the removal of 26.4 kg of iron (94% of the inlet mass flux).

Manganese was not as successfully treated by the wetland: only 8.3% of the 368.5 kg of mass which entered the basin during the entire study period was removed from the flow. During most of this period (October 11 through March 18, fig. 2b) inlet and outlet manganese flux values barely differed except for the December 8 and January 5 sample intervals when the outlet flow carried an additional 5 and 2 kg, respectively. Not until mid-May (fig. 2b) did the system begin to consistently remove manganese from solution, and, as with iron, the June 1 period displayed the greatest manganese removal, retaining 14.2 kg (26%

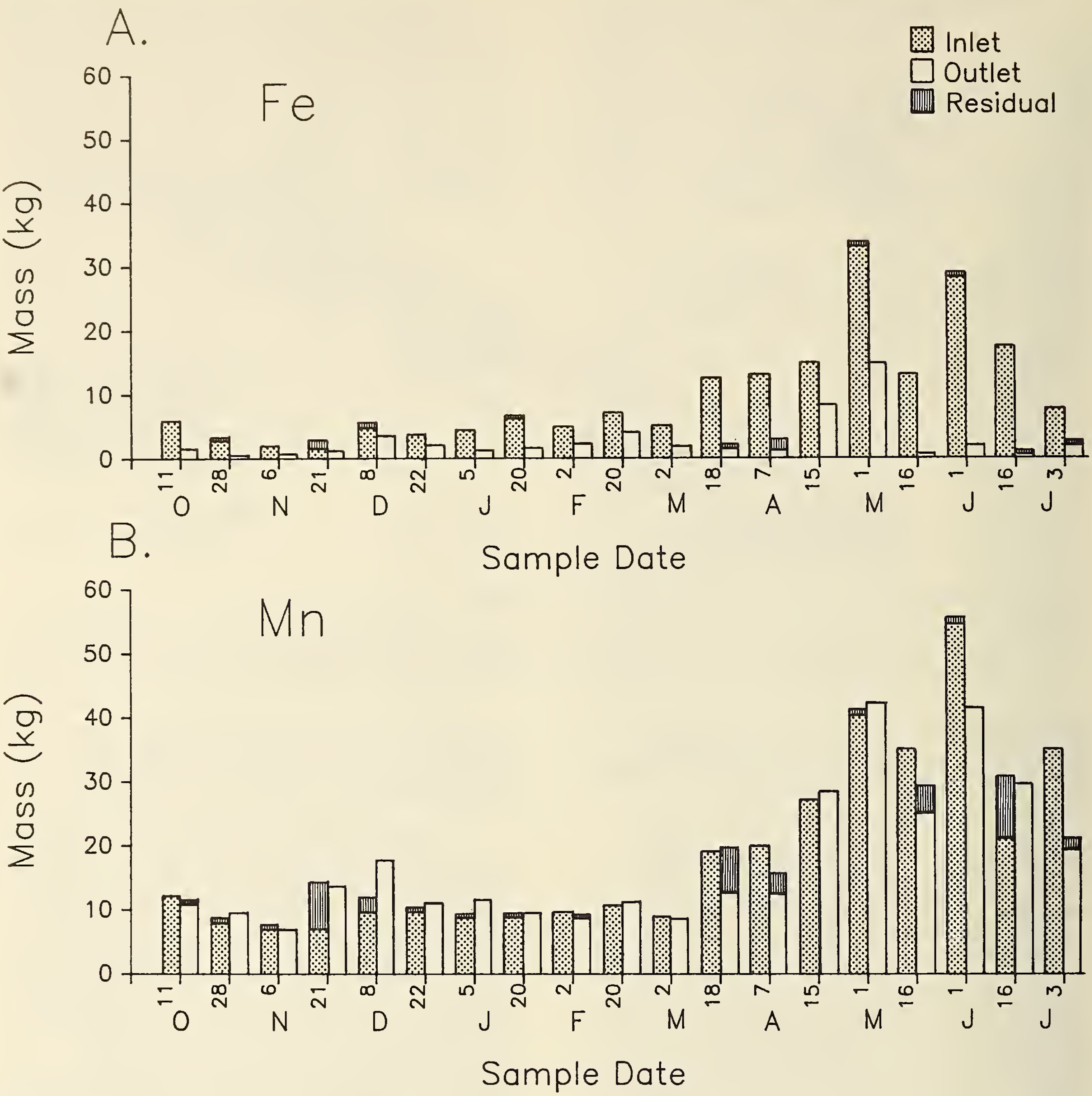

Figure 2.--Inlet and outlet components of the iron (A) and manganese (B) budgets calculated for each sample period.

of the inlet mass concentration) within the wetland. Later, during the July 3 sample period, inlet manganese concentrations were reduced by 40%, a percentage corresponding to the removal of 13.8 kg.

Flow, as suggested by Kadlec (1987), does appear to influence metal removal in a wetland system. The peak inlet flow volume, 20.1 gpm, occurred over the period of April 15 (figs. 3a,c). Peak inlet mass concentrations followed this springtime hydrograph peak: the maximum iron influx of 23.6 ppm occurred on May 1 (fig. 3a), and the maximum manganese influx of 53.9 occurred on June 1 (fig. 3c). This sequence-- peak mass concentrations following after peak flow volumes--could result from the springtime "flushing" of metals from the mine spoil.

The wetland responded to the increased flow volumes by decreasing the percentage of iron removed from its inlet water. During the springtime increase of the inlet hydrograph (March 18 to April 15), the amount of mass removed dropped from approximately 10 kg (80-85% of the inlet mass) for each of the March 18 and April 7 periods, to 6.2 kg (43% of the inlet mass) for the April 15 period (fig.

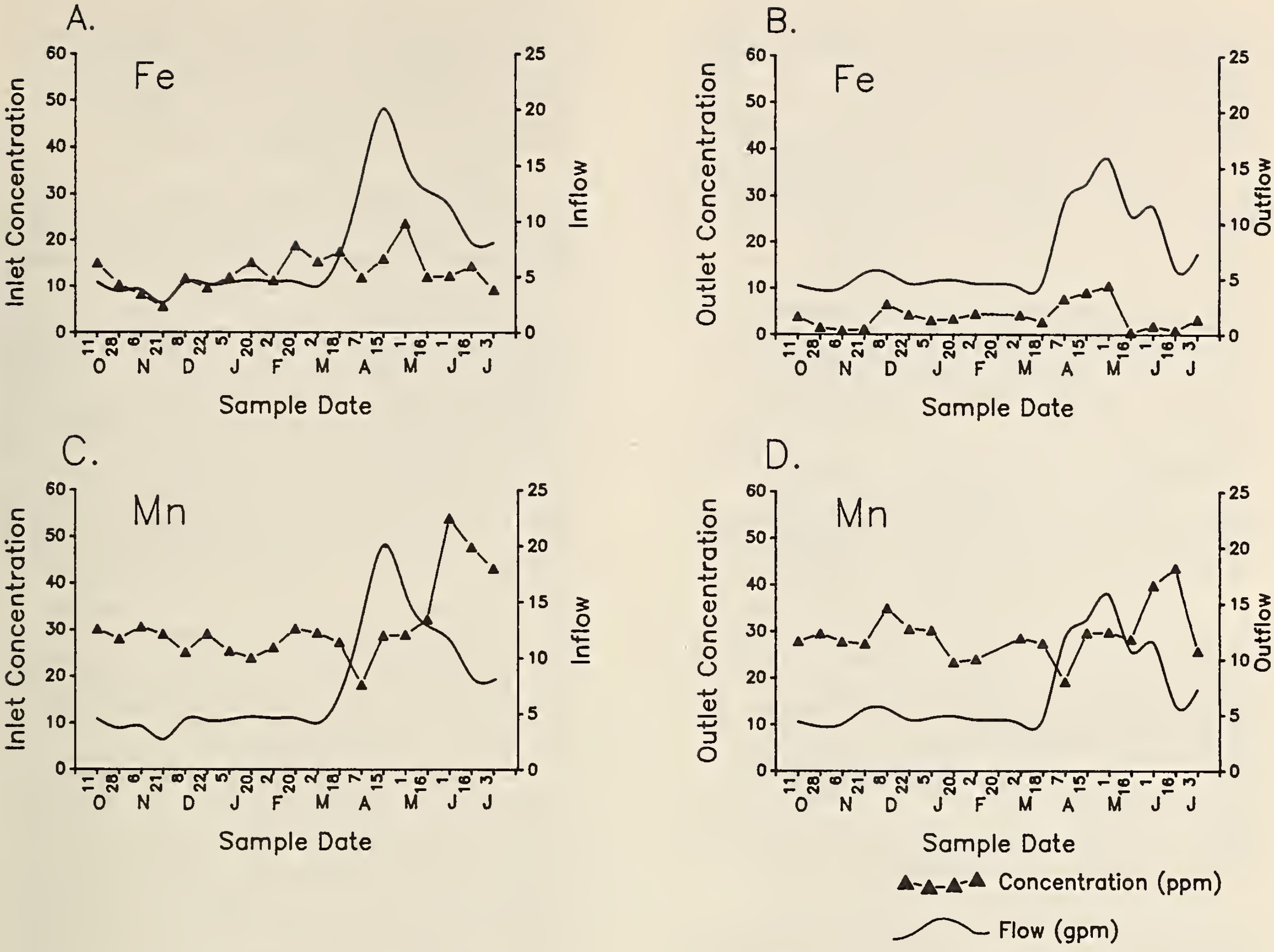

Figure 3.--Inlet and outlet concentrations of iron (A & B), and manganese (C & D), documented for the 10-month study period. Plots of the inlet and outlet hydrographs are included for comparison of flow volumes with mass concentrations.

2a). The amount of iron removed during May 1 increased to 18 kg, but since inlet iron concentrations increased greatly during this period, this removal corresponded to only 55% of the total mass.

The outflow hydrograph exhibited a lower, and more broad springtime peak, suggesting that the increased inlet volume did not immediately flow through the basin, but that a portion of the water was stored within the wetland, and then released at a more constant rate. Iron concentrations at the outlet increased with increasing outflow volume (March 18-May 1, fig. 3b).

During the April 15 period, when the inlet flow was at its highest and percentage iron removal at its lowest, manganese concentrations were slightly higher at the outlet than at the inlet. Mass budget calculations show an extra 0.9 kg of manganese leaving the wetland during the April 15 period, and an extra 1.3 kg leaving over the May 1 period. From May 16 through the end of the study period manganese was removed from the wetland flow. In fact, the greatest amount of removal (14.2 kg) coincided with the largest manganese influx (54.3 kg) during the June 1 period (fig. 2b).

Outlet manganese concentrations were greatest during the intervals of June 1 and June 16, reflecting the high inlet concentrations of those same periods (fig. 3d). The peak outlet concentration of 43.6 ppm did not occur during the same interval as the peak inlet concentration however, instead the outlet peak appeared during following, June 16, period.

The period from March 18 through April 15 was not the only period of rising inlet flow volumes: a small flow increase also occurred from November 21 to December 8 (fig. 3c). The response of the wetland to this flow increase was similar to its response during the springtime flow increase--iron removal dropped from 78% of the inlet mass during November 21 to 43% during December 8, and an extra 5 kg of manganese left the wetland over the December 8 period.

The effects of length and width on the removal of iron and manganese from the surface water were examined with an analysis of variance. Removal was calculated by subtracting the concentration at each grid point from the inlet concentration. Time effects were not examined with these tests; instead, all nineteen samples obtained from a particular location were considered to 'replicate' the average chemical conditions at that area. While width was not found to be significant in the removal of either metal, length was significant in both cases, with iron being more affected. Duncan's multiple range test was used to examine the equality of the column means averaged over the three rows. It indicated that while removal did increase with length, the means for columns 7-11 (refer to fig. 1 for sample grid design) were not significantly different from one another, similarly, the means for columns 5 and 6 were also not significantly different.

A second-order regression analysis of iron removal versus length produced a predicted curve (fig. 4), with a 0.962 r-squared value. While a first-order relationship would also describe the data points, the quadratic curve provides a better fit and also suggests that the rate of iron removal slows during the time it takes water to flow from inlet to outlet. This is a likely possibility since reaction rates can slow as the reactants become more dilute.

The importance of length in the removal of manganese cannot be as clearly defined as with iron. Length was found to be a significant factor, but Duncan's test revealed that the greatest removal occurred in columns 7-9, and that columns 10-11 averaged the same amount of removal as columns 5-6. Factors in addition to length must be influencing manganese removal. The first-order regression of manganese removal versus length (fig. 5) demonstrates this with an r-squared of 0.53; length cannot explain all of the variability in manganese removal. A second-order fit did not significantly improve the r-squared value, and therefore is not presented here.

The two-way interaction of length x width was significant as well, and a plot of the row means per column indicated that three surface locations (designated as [1,7], [1,8], and [1,9] in fig. 1), contained water with less iron and manganese, 37% and 20%, respectively, than water at the outlet. Samples from these areas were also distinguished by an enrichment in K, P, Na, Mg, and Ca. Similar water chemistry, i.e., high nutrient and low dissolved metal concentrations, was also found in the interstitial waters, especially from samples from the lower piezometers located immediately above the limestone layer. Based upon this information, two hypotheses can be made: 1) the high calcium and magnesium values at these three locations were due to the dissolution of limestone, which could have been mixed with the humic layer in these areas during wetland construction, and/or 2) interstitial water, rather than surface water might have been collected at these areas. The second possibility is likely since the wetland surface surrounding these areas can be described physically as a hummocky area where surface water was found in shallow depressions (0.5 to 1.0 inches deep) separated by emergent clumps of cattails, grasses, and saturated soil. Water collected as a surface sample might have actually flowed from the substrate at the time of collection.

SUMMARY AND CONCLUSIONS

An important question concerning this study is, of course: did the wetland

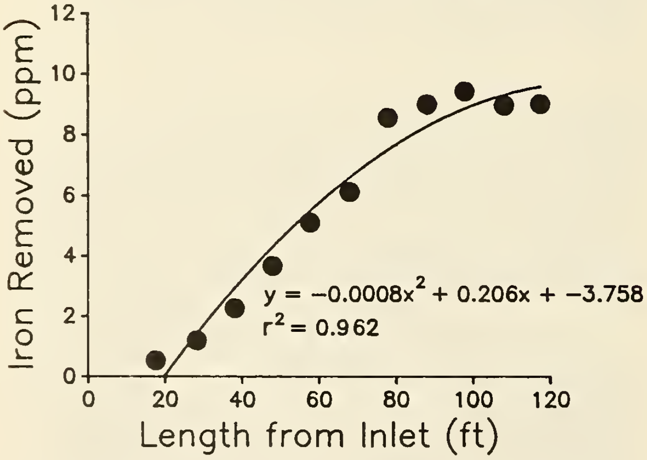

Figure 4.--Plot of the relationship between iron removal and basin length. Each point represents the column average for the 10-month period.

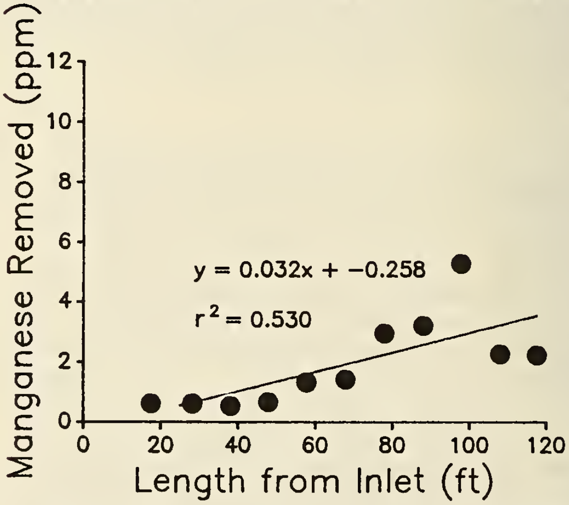

Figure 5.--Plot of the relationship between manganese removal and basin length. Each point represents the column average for the 10-month period.

effectively treat flow from the AMD seep? Effectiveness implies that effluent water quality meets standards set by the Surface Mining Control and Reclamation Act of 1977. Iron concentrations can be no greater than 7 ppm daily, or an average of 3.5 ppm monthly; manganese limits have been set to 4 ppm daily, and 2 ppm for a monthly average (USEPA 1983). Effluent from the wetland met the daily iron requirement at every sampling except for April 7, 15, and May 1, when the inlet flow volumes were higher than average. The monthly standard was met in every month but February, April, and May. Manganese concentrations remained above limitations throughout the entire period. In February, however, the mining company discontinued its downstream chemical treatment of the wetland effluent. Nevertheless, outflow from the polishing pond (fig. 1) still continued to meet iron and manganese requirements for the remainder of the study.

Flow appeared to be an important variable affecting iron and manganese removal: increased flow volumes coincided with drops in in percentage removal of iron and increased outlet manganese concentrations. In addition, peak inlet mass concentrations, and therefore peak outlet concentrations, followed the peak springtime inflow.

The importance of length as a factor which influences wetland treatment abilities agrees with findings from other researchers. A study by Wile et al., (1985) of a municipal waste wetland showed that one system with a length-to-width ratio of 75:1 constantly outperformed another with a 4.5:1 ratio. WAPORA (1983) recommended a ratio of 20:1. Within the present study, the increase of iron effluent concentrations during the spring (fig. 3b) suggests that the system was underdesigned for the maximum mass influx. The relationship between length and iron removal (fig. 4), suggests that a lengthwise extension of the basin would increase iron removal. Although length was not as important in removing manganese, figure 5 suggests that a longer basin would also improve manganese removal.

While outlet concentrations did not always show improvement in water quality, a few surface locations, and the interstitial waters, did exhibit consistently lower iron and manganese concentrations. Interaction with soil, and/or the underlying limestone layer, appears to be a common factor between these spots. A wetland designed with a more permeable substrate might provide greater contact between soil and water, provided water remains shallow.

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CONSTRUCTED WETLANDS FOR ACID DRAINAGE CONTROL IN THE TENNESSEE VALLEY

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Abstract--Constructed wetlands are often a preferred alternative to conventional methods of treating acid drainage at mine sites, coal preparation facilities, and coal-fired power plants. The Tennessee Valley Authority (TVA) has designed and constructed wetlands in Alabama and Tennessee to treat acid discharges from these sources. Between June 1985 and August 1987, seven wetlands were constructed to treat acid drainage at an inactive coal preparation plant and adjacent mined area and four wetlands were constructed at TVA coal-fired power plants. Although site-specific characteristics often restricted use of standardized methods, generic design, construction, and operation guidelines have been developed. Treatment efficiencies have ranged from 82% - 99% removal for total iron and 9%- 98% removal for total manganese. Preliminary design guidelines for required treatment area were: ph < 5.5 s.u., 2.0 m^2/mg Fe, 7.0 m^2/mg Mn; pH > 5.5 s.u., 0.75 m^2/mg Fe, 2.0 m^2/mg Mn. Wetlands systems costs from design to operation averaged \$12.18/m^2 of treatment area.

INTRODUCTION

Acid mine drainage is generated by the oxidation of iron sulfides in mine spoil, producing water that is acidic, with high concentrations of iron (Fe), sulfate, and other objectionable constituents, including manganese (Mn), aluminum, suspended and dissolved solids, color, and hardness (EPA 1971; Caruccio and Giedel 1985). Although stoichiometry may be somewhat different, acid drainage from ash ponds at coal-fired power plants is similar to acid mine drainage.

Though effective, conventional acid drainage control techniques, such as chemical treatment or land reforming, are costly and generally require long-term maintenance. Constructed wetlands appear to offer an inexpensive, self-maintaining, long-term solution to treating acid drainage of moderate flows and chemical concentrations. The ability of wetlands to remove pollutants from acid drainage has been demonstrated by several investigators (Wieder et al. 1984; Guertin et al. 1985; Brodie et al. 1987). Various researchers have explored design and operational parameters of constructed wetlands for treating acid drainage (Hammer and Kadlec 1983; Pesavento 1984; Huntsman et al. 1985; Girts and Kleinman 1986; Wieder and Lang 1986).

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The Tennessee Valley Authority's (TVA) first constructed wetland for acid drainage treatment, known as Impoundment 1, was located at a reclaimed coal preparation plant site in northeast Alabama (Brodie et al. 1987). Success of this wetland at meeting permit effluent limitations has led to the construction of 11 wetland treatment systems at TVA coal facilities and coal-fired power plants, and to an extensive research program on constructed wetlands. This paper summarizes TVA's constructed wetlands treatment systems and offers preliminary design guidelines based on results to date.

TECHNIQUES

Site characteristics often restricted use of standardized methods; therefore, wetlands were designed for specific conditions. A generic description of pre-design investigations through wetlands operation follows.

Pre-design

State regulators generally met onsite with TVA officials to review alternative sites and treatment options. Wetlands systems were approved as long as all effluent discharge limitations were to be met (i.e., total Fe < 3.0 mg/L, total Mn < 2.0 mg/L, pH = 6.0 - 9.0 s.u., and nonfilterable residue < 35.0 mg/L). Therefore system designs ocassionally included a final cell to provide for chemical treatment if necessary.

Wastewater characterization and site hydrology were the two most important pre-design data needs. Pre-construction water quality sampling was conducted for all flows to be treated and any streams that would be affected by the wetlands. Analyses included pH, Eh, total and dissolved Fe and Mn, nonfilterable residues (NFR) and total dissolved solids, sulfate, aluminum, dissolved oxygen, manganese, zinc, selenium, mercury, and cadmium. Flow monitoring was incorporated into baseline site monitoring and compared to existing flow data and hydrologic modeling. Baseline population estimates of aquatic biota in receiving streams were estimated to provide a means of documenting stream recovery.

Often it was necessary to locate the wetland off the immediate area or leased/owned surface, thus negotiations with landowners for initial access and long-term future control were conducted. TVA owned or purchased many of the wetland sites but also pursued other surface control arrangements including long-term leases and permanent easements.

Regulations neither specifically addressed nor gave guidance on constructing treatment wetlands. Permits and approvals for wetlands construction required from State and Federal regulators included a National Environmental Policy Act review, floodplains (Executive Order No. 11988) review, National Pollutant Discharge Elimination System permit, surface mining permit, and a water engineering report.

Topography was determined in sufficient detail to plan the number and location of cells to minimize cut and fill requirements dictated by a particular gradient. Because site regrading was usually an early step in wetlands construction, topography was completely altered, and detailed (e.g., 2-foot contour interval) topographic surveys were not warranted.

Geology was evaluated to determine if the site overlay shallow bedrock or lacked suitable growth media. If necessary, sources of borrow and adequate growth media were identified. Flow patterns and depth of groundwater were determined to identify inflows or outflows that could affect water quality or hydrologic balance.

Preferred sources of emergent vegetation for transplantation were nearby natural wetlands developed in similar quality water to avoid stress from abrupt changes in edaphic conditions. Cattail (Typha), followed by Scirpus, Eleocharis, and Carex were the most tolerant, readily available species for transplantation. A rush Juncus was used with less success. Preliminary research results (S. R. Copeland, unpubl. data) suggested that Typha latifolia and Eleocharis quadrangulata provided higher radial oxygen loss than other common species, thereby enhancing substrate redox conditions to bind insoluble forms of metal precipitates in the substrate.

Design and Construction

Size of wetlands, number of cells, spillways, and dike specifications were designed for 10-year, 24-hour storm event estimated from site flow monitoring or various methodologies (Lyle 1987). Erosion and sedimentation control structure design and construction (EPA, 1976; USDA, 1982), along with best engineering estimates and practices were used for those components having no design guidelines.

TVA's constructed wetlands ranged in size from 3.5 m^2 (38 ft^2) to 113.0 m^2 (1216 ft^2) per average flowing liter per minute, and 2.0 m^2 (22 ft^2) to 41.0 m^2 (441 ft^2) per maximum flowing liter per minute. Design sizes were dependent on water quality characteristics, storm flow hydrology, and land availability. Wetlands were designed to accommodate stormflow, then increased in size if very poor quality water was to be treated. Increasing the size of a wetland up to twice the stormflow design area only modestly increased costs and provided adequate treatment area.

Wetlands shapes varied because of existing topography, geology, or land availability. Irregular shapes for wetlands cells enhanced natural appearance and provided hydraulic discontinuity. Configurations that increased velocities causing channelization, scouring, bank erosion, etc. were avoided.

Number of cells for constructed wetlands was determined by site topography and hydrology. Level sites were amenable to large cells hydraulically chambered with rock or earthen finger dikes, large logs, vegetated hummocks, or other baffles. Steeper gradients required more grading or a system of several cells terraced down slope.

Water depth and bottom slope were dependent on plant species, pollutant concentrations, freeze potential, and desired longevity of the system. Typha latifolia has been the preferred species in TVA constructed wetlands. Other plants used in shallow water include Scirpus, Juncus, Carex, Eleocharis, and Equisetum. Excessive water depths not only inhibited desirable species development, but promoted anoxic, reducing conditions in the water column seriously affecting the oxidation of iron and manganese. Shallow water depths which are subject to freezing in more northern climates are suitable in the Tennessee Valley. The primary advantages of shallow water is to enhance oxygenation and increase plant production. Potential disadvantages are reduced storage capacity and retention time. Average water depth in TVA's wetlands ranged from 15-30 cm (6-12 in) with some shallower and some deeper areas to provide for species diversification. A few deep pockets of one meter or greater were included in many cells to provide recharge zones and aquatic fauna refuge in drought events.

Most wetlands were completed in early summer, although successful installations were completed as late as October. Wetlands construction began with clearing the site, followed by grading and dike construction, and importing suitable materials as necessary to meet design specifications. Brush was burned or pushed along the site perimeter to provide wildlife habitat. Spillways were either rock-lined or covered with non-biodegradable erosion control matting and planted with Scirpus, Carex, or grasses. Water level control or flow monitoring devices were incorporated into the spillway design and construction.

Vegetation was hand-dug to obtain complete root balls/rhizomes. Transplantation was completed on the same day as digging, and plants were not subjected to extreme temperatures, drying, or wind during transport. Typha was set into the substrate at about nine plants /m^2 and stems broken over above the water level to prevent windfall and to stimulate new growth from the rhizomes. Bulrush clumps were simply placed in the desired location.

Wetlands were fertilized with a phosphorous-potassium fertilizer such as 0-12-12 at 400 kg/ha (353 lb/ac). Mosquito fish (Gambusia affinis) were stocked for insect pest control.

Operation and Maintenance

Post-construction activities included effluent monitoring, fertilization, and maintenance of dikes, spillways or other control structures and pest control. Effluent monitoring was performed several meters downstream of the final spillway so that any leakage was included in the sample. Monitoring requirements included pH, total Fe and Mn, and NFR. Additional water chemistry and biological monitoring were used to quantify wetlands treatment efficiencies and wetlands habitat benefits. After the first year, fertilization was done only if vegetation showed signs of nutrient depletion. Dike repair due to muskrate burrowing was required at one wetland. Army worm (Simyra henrici) infestations at another required control measures to prevent eradication of cattail.

RESULTS

A summary of characteristics and water quality parameters for TVA's 11 constructed wetlands is presented in Table 1. Dates of initiated operation are based on the first time effluent monitoring began (i.e., usually within one week of initial dischange). Areas are given as surveyed inundated area. Influent water chemistry, in most cases, is based on at least one year of seasonal sampling of contributing seeps. Effluent monitoring, including flow, is generally based on twice monthly discharge permit sampling results from the date on which the wetland system began operating.

TABLE I

TVA ACID DRAINAGE WETLANDS TREATMENT SUMMARY

Wetlands System	Date Initiated Operation	Area m^2	Number Cells	Influent Water Parameters (mg/L)				Effluent Water Parameters (mg/L or L/min)						Treatment area m^2/mg/min	
												Flow			
				pH	Fe	Mn	NFR	pH	Fe	Mn	NFR	Ave	Max	Fe	Mn
W C 018	6-86	4800	3	5.6	150.0	6.8		3.9	6.4	6.2		70	1495	0.2	4.2
King 006	10-87	9300	3	4.2	153.0	4.9	40.0					379	2271	0.2	5.0
Imp 4	11-85	2000	3	4.9	135.0	24.0	42.0	4.6	3.0	4.0	6.0	42	49	0.4	2.0
950 NE	9-87	2500	2	6.0	11.0	9.0	19.0	6.6	0.5	0.2	49.0[1]	348	1673	0.7	0.8
R T - 2	9-87	7300	3	5.7	45.2	13.4		6.7	0.8	0.2	2.0	238	681	0.7	2.3
Imp 2	6-86	11000	5	3.1	40.0	13.0	9.0[2]	3.1	3.4	14.0	0.8[2]	400	2200	0.7	2.1
Imp 3	10-86	1200	3	6.3	13.0	5.0	28.0	6.8	0.8	1.9	4.7	87	379	1.1	2.8
W C 019	6-86	25000	3	5.6	17.9	6.9		4.3	3.3	5.9		492	6360	2.8	7.4
950-1 & 2	1976	3400	3	5.7	12.0	8.0	20.0	6.5	1.1	1.6	5.4	83	341	3.4	5.1
Imp 1	5-85	5700	4	6.3	30.0	9.1	57.0[3]	6.5	0.9	2.1	2.8	53	227	3.6	11.8
Col 013	10-87	9200	5	5.7	0.7	5.3		6.7	0.7	13.5		288	408	45.6	6.0

[1] – one effluent sample to date
[2] – one sample, July 1987
[3] – from preconstruction instream sample

Impoundment 1 was TVA's first constructed wetland, treating acid seepage from a coal slurry pond dike at the reclaimed Fabius Coal Preparation Plant in Jackson County, Alabama. Dominant vegetation is *Typha*, with *Scirpus*, *Leersia*, *Juncus*, *Eleocharis*, *Utricularia*, and *Sparganium* among a total of 41 species present two years after construction. Since construction, Impoundment 1 has produced compliance quality effluent.

Impoundment 4, also at the Fabius plant site, was built to treat acid seepage emanating from process water recirculation ponds. These ponds (pH = 3.5 s.u.) were reclaimed in 1986 and the inflow to Impoundment 4 has been limited. Dominant plants are *Typha* and *Scirpus*. The original planting of Impoundment 4 took place in November 1986. Few plants survived in spring and the wetland was replanted the following July. A sodium hydroxide (NaOH) treatment system was installed to augment the wetland treatment because of the extremely low pH of the seepage.

950-1 and 2 was a two-cell sedimentation basin receiving mine acid drainage from the reclaimed TVA Fabius 950 coal mine in Jackson County. A *Typha* marsh has naturally developed in the upstream cell with expansion into the lower cell. Treatment with NaOH, required from 1976 to 1984, has been discontinued. The discharge was released from NPDES permit monitoring requirements in 1987.

Impoundment 2 is a series of constructed wetlands intermediate in a 138 ha (341 ac) drainage basin receiving acid drainage from non-TVA abandoned mine land and the coarse refuse disposal area at the Fabius plant site. Effluent from the wetlands is treated with sodium hydroxide and discharged. Vegetation in the wetlands is predominantly *Typha*.

Widows Creek 018, located at TVA's Widows Creek Fossil Plant in Jackson County, receives seepage from an abandoned ash disposal area. The wetland was adjacent to a leaking coal pile runoff pond (pH = 2.8 s.u.) that has caused adverse effects on water quality and vegetative development. Dominant vegetation is *Typha*. An NaOH treatment system was installed at this wetland for pH increase.

Widows Creek 019 also receives acid seepage from abandoned ash disposal areas. Widows Creek Fossil Plant's operational needs at this site have resulted in plans to flood the wetland

and install a facility to pump water to an existing treatment system. Effluent data may reflect additional seepage within the wetlands system and should be viewed with caution.

Impoundment 3 is located at the TVA 950 coal mine and receives acid mine drainage. It was constructed to replace a chemical treatment system which operated from 1976 to 1986 and has produced compliance quality effluents since construction. Dominant vegetation is *Typha*.

Rocky Top 2 is located at TVA's reclaimed Fabius Rocky Top coal mine in Jackson County. Inflow is acid mine drainage and dominant vegetation is *Typha*.

950 NE is located adjacent to the TVA 950 coal mine and receives acid mine drainage from about 32 ha (79 ac) of reclaimed area. Dominant vegetation is *Typha*; only minor discharge has occurred since construction.

Kingston 006 is located at TVA's Kingston Fossil Plant in Roane County, Tennessee. It was constructed to treat acid seepage and runoff from active ash disposal areas. Dominant vegetation is *Typha*. About 20 cm (8 in) of high-calcium, minus 16 mesh limestone covered with about 30 cm (12 in) of spent mushroom compost for vegetative substrate was included in the final cell of the wetland system (B. G. Pesavento, pers. comm.).

Colbert 013 is located at TVA's Colbert Fossil Plant in Colbert County, Alabama. It receives acid drainage from an indefinite source near an active ash disposal area. This wetland is still under development and is dominated by *Typha* and *Scirpus*.

Water quality improvement has occurred at all of the operating constructed wetlands. Five systems have produced dramatic results and have apparently mitigated some of TVA's most stubborn pollution problems. Where regulatory limits were not entirely achieved, cost savings were realized in a reduction in chemicals needed for further metals precipitation or pH adjustment.

Total costs for construction of nine wetlands treatment systems are shown in Table 2. Overall average cost was \$12.18/m^2 (\$1.13/ft^2) of treatment area. Costs for 9 wetlands are best exemplified by the Impoundment 3 project, which cost \$40,000. Total cost consisted of about 20 percent for design and project management, 35 percent for equipment and supplies, and 45 percent for labor. Because TVA was annually spending \$12,000 to \$15,000 for chemicals and \$10,000 for pond maintenance that failed to maintain complying discharges, the wetland system, with an annual operation and maintenance cost of \$1,000, has proven cost-beneficial within one year.

CONCLUSIONS

Constructed wetlands offer a preferred alternative to conventional methods of treating acid drainage from certain coal-related sources. TVA has constructed 11 wetlands for treating acid drainage and has developed guidelines for design, construction, and operation of the systems. Six of these constructed wetlands allowed TVA to discontinue chemical treatment for Mn and Fe removal and pH adjustment. Two systems were under development but were expected to produce compliance quality effluents by mid 1988. The remaining wetland systems, although not treating water to compliance levels, removed significant amounts of metals from the influent, reducing chemical treatment costs. As more wetlands are constructed for acid drainage treatment, and as research results become available, design criteria will no doubt be improved.

However, numerous wetlands treatment systems are planned or under construction in the coal and utility industries. Our experience suggests the following preliminary general guidelines for Fe and Mn treatment area requirements for desired discharge levels of Fe = 3 mg/L or less and Mn = 2 mg/L or less

Fe: $2\ m^2/mg < pH\ 5.5 > 0.75\ m^2/mg$
$(21\ ft^2/ppm < ph\ 5.5 > 8\ ft^2/mg)$

Mn: $7\ m^2/mg < pH\ 5.5 > 2\ m^2/mg$
$(75\ ft^2/ppm < pH\ 5.5 > 21\ ft^2/ppm)$

For pH levels of less than 5.5 s.u., suggested treatment area for Fe would be 2 m^2/mg/min (21 ft^2/ppm) and for Mn 7 m^2/mg/min (75 ft^2/ppm). For pH levels above 5.5 s.u., suggested treatment area for Fe would be 0.75 m^2/mg/min (8 ft^2/ppm) and Mn 2 m^2/mg/min (21 ft^2/ppm). For example, a seep with 50 mg/L Fe, 15 mg/L Mn, pH 5.6 s.u., and an average flow of 113 L/min (30 gal/min) would require:

For Fe, the rate factor is .75 m^2/mg/min.

Area of treatment =
$0.75\ m^2/mg/min)(113\ L/min)(50\ mg/L) = 4237.5\ m^2$

For Mn, area =
$2\ m^2/mg/min)(113\ L/min)(15\ mg/L) = 3390\ m^2$

and the wetlands treatment system area should approximate 4200 m^2 (45,200 ft^2 i.e., about 1 acre).

TABLE 2

WETLANDS SYSTEM CONSTRUCTION COSTS

Wetlands System	Area ha	% Equip	% Labor	% Overh	Total ($000's)	$/m^2	$/ft^2
R T - 2	0.7	32.6	53.4	14.0	26.4	3.58	0.33
Imp 2	1.1	70.2	12.3	17.5	57.0	5.25	0.49
W C 018 & 019	2.9	-	-	-	209.0	6.98	0.65
Imp 1	0.5	19.0	49.6	31.4	42.9	7.46	0.69
950 NE	0.3	38.1	46.0	15.9	35.2	13.80	1.28
Imp 4	0.2	28.2	26.8	45.0	28.0	14.12	1.32
King 006	0.9	28.6	43.3	28.1	131.7	14.21	1.32
Imp 3	0.1	34.8	43.5	21.7	40.2	32.03	2.98

average cost = $12.18/m^2 = $1.13/ft^2

These treatment area estimations do not include storm flow hydrology and size of constructed wetlands must be increased, if necessary, to accommodate storm events and prevent dike or spillway damage.

Obviously all of the above generalize numerous factors, i.e., temperature dependent rate constants, hydraulic loading, retention time, surface area for microbial growth, length, width, depth and slope of system, etc., for which we have limited information. Incorporation of these factors and development of an expression relating influent values for Fe, Mn, pH, and flow to desired effluent values and recommended treatment area, hydraulic loading, and retention time is underway and will be reported later.

Although our results are encouraging and we suspect that properly designed and constructed wetlands treatment systems will function for long time periods, better documentation is obviously needed. TVA has initiated research addressing basic design questions, including optimum substrates and vegetation, hydraulic and contaminant loading rates, treatment system capacity and longevity, storm event and ground water monitoring, and limestone bed design (Brodie et al. 1988).

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THE SIMCO #4 WETLAND: BIOLOGICAL PATTERNS AND PERFORMANCE OF A WETLAND RECEIVING MINE DRAINAGE. I[1]

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S. Edward Stevens, Jr., Kim A. Dionis, and Earl R. Murphy [2]

Abstract.--In 1985 a 3,000-m^2, three-celled wetland was installed at the Peabody Coal-American Electric Power Simco #4 deep coal mine site near Coshocton, OH. The wetland included a limestone/compost substrate planted with Typha latifolia L. (cattail). The deep mine seepage pH is near 6.0, total iron 80-241 mg/L, and acidity 15-389 mg/L. The percent reduction in iron concentration in effluent water relative to influent water of the wetland significantly exceeded pre-wetland percent reduction, improving from 28% during the first winter after construction to 62% in the summer of 1987. Further site modifications in 1987 elevated the percent iron reduction of the wetland to 70-85%. Iron reduction corresponds to greater wetland area, higher cattail density and increased plant coverage. Prominent plants in the wetland besides cattail are Leersia oryzoides (L.) Sw. (cutgrass) and several algal species. Cattail and cutgrass coverage increased from 1986 to 1987. Roots of cattail accumulated up to 5 times the iron content of roots from a control site.

INTRODUCTION

In the last 10 years over 100 wetlands have been constructed in the coal-bearing regions of Ohio, Pennsylvania, Maryland, and West Virginia in attempts to treat acidic mine water (Kleinmann and Girts 1987). The alternative can be costly: chemical treatment in settling ponds may cost a mining company as much as \$50,000/year. Usually acidic mine water exceeds Federal regulations for iron (3 mg/L), manganese (2 mg/L), pH (6-9), or a combination of these. Sulfates and acidity can also be high. Wetlands have shown promise in lowering levels of iron and manganese (Wieder et al. 1982; Brooks et al 1985). Monitoring the performance and composition of some of these wetlands will return useful knowledge on their potential.

WETLAND CONSTRUCTION AND MODIFICATIONS

The Simco #4 underground mine began operation in 1970 and ceased operation on October 20, 1978. The location of the portal was a pre-existing strip bench operation of 1961. This mine operated 3 conventional sections mining the Kittanning coal seam. Run-of-mine coal was delivered to the Columbus & Southern Ohio Electric Conesville Generating Station.

Upon abandonment the mine was left unsealed and the highwall above the portal was not reclaimed to approximate original contour. In May 1979 the Division of Mines and the Mine Safety and Health Administration approved plans for sealing the Simco #4 underground mine. The drift openings were sealed with 24 in. concrete or concrete bulkhead constructed with pilasters. One pilaster was used for widths under 16 ft. and two pilasters were used for widths greater than 16 ft. The seals were built into the floor, ribs, and top, and the tops were supported to make the areas safe prior to construction. All three openings at the Mine #4 portal were sealed using this procedure, and the pre-existing highwall was subsequently backfilled.

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In 1980, water treatment began for discharge seepage that developed from the mine near the base of the backfill. Discharge specifications were met by treating with soda ash briquettes. During the next several years, the flow increased to approximately 120 gpm while the water quality remained poor during the period 1980 through 1985: pH, 5.7-6.3; total iron, 145-241 mg/L; total manganese, 3.1-6.0 mg/L; and acidity, 140-389 mg/L.

As the flow increased it became increasingly difficult to treat the discharge effectively with soda asd briquettes. In an attempt to improve the treatment system and lower treatment costs, Simco/Peabody decided to use caustic soda and install an aeration system to elevate pH and enhance the settling of iron and manganese.

From March 1980 through June 1985 Simco/Peabody studied several options to effectively seal the mine to eliminate the discharge. One such method proposed sealing the Simco #4 underground mine with fixed Flu Gas Desulfurization Sludge from the Columbus & Southern Ohio Electric Conesville Generating Station. However, both the Office of Surface Mining Reclamation and Enforcement and the Ohio Environmental Protection Agency raised numerous questions and informational requests on the use of scrubber sludge. Concern was expressed about the long-term liability of the sludge if it were to become hazardous by decree or demonstration and also over the sludge fixation agent.

It was thought that the proposed innovative sealing scheme may elicit a response from the regulatory agencies relieving liability and setting up a cooperative research effort; however, this did not happen. Since the Simco #4 underground mine was under Notice of Violation (NOV) for its discharge, Peabody Coal developed cost estimates for the double bulkhead seal with center plug (the more conventional approach).

Complicating the water discharge problem was an NOV issued by the Ohio Department of Natural Resources (ODNR), Division of Reclamation. The NOV issued May 1983 required Simco/Peabody to remove all treatment equipment, ponds, and totally reclaim the area. Otherwise, final bond release could not be obtained and the permit could be revoked. Abatement extensions were granted by ODNR while Peabody did further development on sealing methods. While the plans to reactivate the entries and construct hydraulic seals within the mine were developed and final construction details and bid requests were prepared, it was decided that such sealing was too costly, time consuming, and would not provide any assurance of complete effectiveness.

Therefore, in April 1985, Peabody Coal contacted a wetland consultant, B. Pesavento, to perform a site evaluation of the abandoned Simco #4 underground mine. His analysis indicated that a wetland could be constructed that would sufficiently improve the discharge, bringing it within applicable discharge limits without the use of the existing treatment equipment. A proposal based upon Pesavento's recommendation was submitted to the ODNR in July 1985. After careful review the ODNR permitted the installation of the wetland as a possible alternative to hydraulic sealing of the mine.

Site conditions at the mine were conducive to construction of a wetland treatment system. The abandoned strip pit west of the backfilled portal area through which the discharge (120 gpm) passed provided more than adequate area and sufficiently low slopes for construction of a wetland system. The pit floor was graded and a layer of crushed limestone (6 inches thick) was applied in the initial stages of wetland construction. The crushed limestone was covered with an organic-rich, deep-rooting medium (18 inches) in which lime was incorporated. Typha rhizomes were planted with a density of $3\text{-}4/m^2$.

The wetland system was constructed in segments (cells) to provide proper gradients to restrict flow velocities and to promote uniform water dispersal throughout the wetland. Segmenting the wetland provided a gradual introduction of the discharge water into the wetland, allowing the vegetation to establish prior to the introduction of the entire discharge.

Construction of the wetland was started on October 14, 1985 and completed 20 November 1985. Three wetland cells separated by mixing pools were established (fig. 1). The total wetland area is about 3,000 m^2. Water quality, vegetation, and aerobic microbial populations have been monitored since June 1986, and are reported herein.

Periodically the wetland has been limed and/or fertilized with phosphate (table 1) in an attempt to increase iron removal and promote the growth of algae. Such applications have now stopped. Despite the liming, pH was unaffected, and the iron removal efficiency of the wetland did not change significantly. However, the iron removal efficiency of the ditch below the wetland was distinctly elevated in the summer of 1986, coinciding with the largest application of lime. Phosphate applications were relatively small.

During the second winter after installation (1986-7) the water below the wetland at station DNO2 required chemical treatment to remove more iron. At the time the water level and flow rate was judged to be too high in Cells 1 and 2, and the use of diversion ditches was recommended to effectively cut flow rate in half and lower the water depth. In addition, a series of hay bale dikes was recommended to be installed as baffles to increase retention time and promote bacterial activity. These changes were completed on September 1, 1987 (fig. 2). By this time the wetland had improved enough in efficiency to discontinue chemical treatment. However, recent analyses show the wetland to be performing at its highest efficiency, with respect to iron removal, since installation.

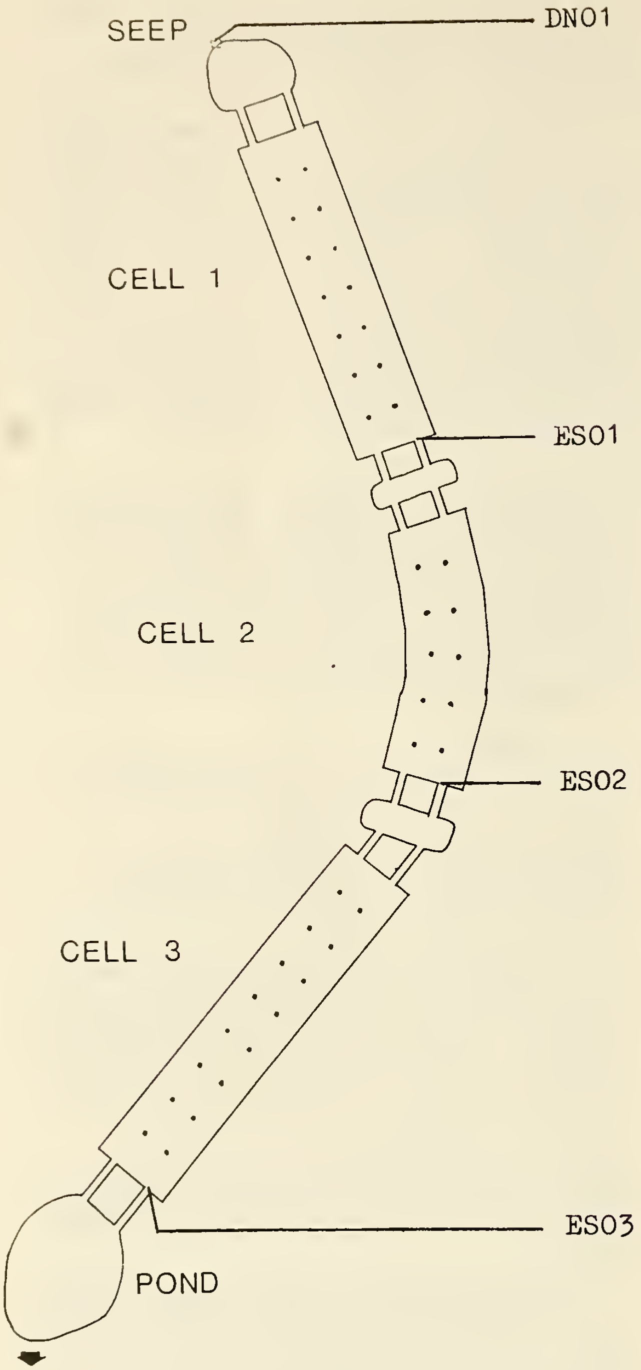

Figure 1.--Diagram of Simco #4 Wetland showing water sampling points at right. Dots represent permanent quadrat stations. Water sampling point DNO2, not shown, is approximately 100-m below pond outlet. Cell areas: Cell 1: 1,008 m^2; Cell 2: 864 m^2; Cell 3: 1,200 m^2.

Table 1.--Dates and amounts of agricultural lime and phosphate (di-ammonium phosphate:0-45-0) applied to the wetland.

Date	Lime (lbs)	Fertilizer (lbs)
Dec 1985	--	200
Feb 1986	--	200
Mar 1986	--	200
Jul 1986	8,000	--
Nov 1986	950	200
Dec 1986	1,000	200
Jan 1987	--	150
Apr 1987	--	150
Jul 1987	--	150
Sep 1987	--	150

METHODS

Water Chemistry

Water was collected by Peabody Coal at 2-3 week intervals at the seep, the outfall of each of the three wetland cells, and 100 m downstream of the wetland, just prior to entering the treatment pond. Water was analyzed by the Peabody Coal Lab for acidity, total iron, total manganese, and sulfate. In the field, pH, temperature, and the water flow rate discharging from the wetland were taken. Acidity was determined using an Orion 407/A pH meter by titration (APHA 1980). Metal concentrations were determined with a Perkin/Elmer 4000 and 5000 atomic absorption spectrophotometer using standard techniques. Sulfates were determined turbidimetrically using a Hach Turbidimeter Model 2100A (through July 1987) and a Hach Ration Turbidimeter Model 18900 (August 1987 on).

On a quarterly basis The Pennsylvania State University (PSU) collected water samples at the permanent sampling stations established within the wetland (fig. 1). These were then filtered (0.45 µm) and acidified (HNO_3) in the field and analyzed by atomic absorption spectrophotometry using a Buck 200 AA for determination of dissolved iron and manganese.

Vegetation

Vegetation was surveyed by PSU at each of the 40 permanent sampling stations on a quarterly basis beginning in July 1986. Canopy coverage was estimated (Daubenmire 1970) in the summers of 1986 and 1987, the first two growing seasons for the wetland. In 1987 algal presence (January) and cover (April) in each quadrat were

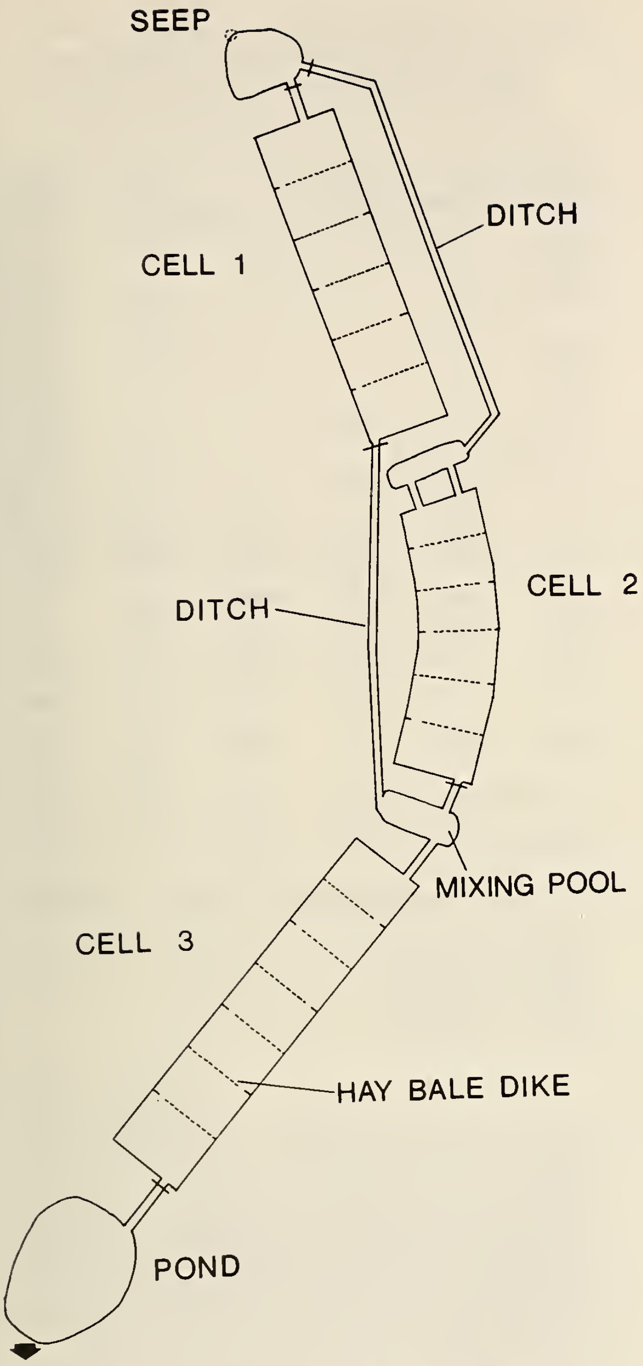

Figure 2.--Diagram of Simco #4 Wetland after site modifications of August 31, 1987. Hay bale dikes were spaced at approximately 35-ft. intervals.

recorded. In addition, the number of cattail shoots was counted in the quadrats in April and August 1987.

Metals in *Typha* Structures

Whole cattail plants were collected in April and August 1987 and returned to the lab in plastic bags. These plants were then separated into leaf blades; leaf bases; inner, outer and entire rhizomes; and roots. Damaged or dead plant parts and visible contaminants were removed, followed by cleaning in tap water, with vigorous rinses and gentle brushing to remove dislodgeable surface contaminants. Samples were then oven-dried at 70°C, ground in a Wiley mill, and stored in sealed glass jars. Wet acid digestion was used, modified from the procedures in Allen et al. (1986). The dried plant material (500 mg) was acid digested at 160°C, first with 10 mL dH_2O (distilled water) and 5 mL concentrated H_2SO_4 for 20 minutes, then 5 mL concentrated HNO_3 was added and digestion continued for 10 minutes. After cooling, samples were filtered (Whatman GFC glass filters), diluted to a volume of 100 mL using deionized distilled H_2O, and stored at 2°C. Two aliquots of each digestate were analyzed by atomic absorption spectrophotometry for iron and manganese concentrations. Each value reported represents an average of the two aliquots. Control plants were collected from a non-impacted site near DuBois, PA and analyzed as above.

Microbial Studies

The microbiological work has essentially been an attempt to discover the major nutritional types of microorganisms present in the wetland, their total number, and their diversity. Until recently heterotrophic microorganisms were not thought to occur in high iron-loaded waters. However, Wichlacz (1980) showed that acidophilic heterotrophs were present in acid mine waters, a result confirmed by McHerron (1986).

Samples were collected in September 1986 and in January, April, and October 1987 at 20 locations along the length of the wetland. Depending on the nature of the sediments, samples were obtained in one of two ways. If the sediments were solid enough to hold a shape, solid cores were taken with a 3-cm-diameter metal cylinder. If the sediments were loose and watery, samples were collected by holding a sterile test tube just below the surface of the sediment, in front of the flow. When the tube was uncapped, the sediments flowed into the tube with as little disturbance as possible. The samples were kept on ice during transportation to the laboratory.

For solid core samples, the outer portion of the core was removed with a sterile razor blade to expose the inner, presumably undisturbed, portion. A subsample of 2.5 g was blended in a Waring blender with 1% sodium pyrophosphate (Balkwill 1977). The purpose of this step was to release the microorganisms from the soil particles; sodium pyrophosphate aids in breaking up the soil aggregates. If the test tube samples were watery, the sediments were blended with enough sodium pyrophosphate to give an approximate 1% solution. From this point on, both types of samples were treated in the same manner.

The suspensions were immediately diluted using sterile distilled in a series of 1:00; 1:1,000; 1:10,000; and 1:100,000. Each dilution tube was placed on a vortexing machine before any liquid was drawn from it so the particles did not have time to settle out. All transfers were made with micropipettes. Each dilution was then plated out in triplicate on seven different kinds of agar media. The media used ranged from very simple and defined (agar water and inorganic media) to complex and undefined (PTYG and BHI), in order to select for a gradient of nutritional types (Balkwill and Ghiorse 1985). Both iron-supplemented and manganese-supplemented inorganic media were used to select for iron and manganese oxidizers. Plates were surface inoculated and incubated at 27°C.

Colonies were counted and described for plates on which 30-300 colonies developed. The counts included fungi, actinomycetes, and bacteria. The final counts and descriptions were made at 15-30 days, depending on the type of medium used. A series of counts was also made within this time period to estimate growth rates (data not presented). Colony types were distinquished on the basis of relative size, color, conformation, border, and elevation. The presence of iron or manganese oxidizers was determined visually by the formation of a deep blue color after flooding the colonies with 0.2% tetramethyl benzidine in 2M acetic acid (Stone 1984). The iron and manganese oxidizers were isolated from these plates for further study. Gram stains were performed on the predominant colony types, and cellular morphology was described.

RESULTS

Water Chemistry

Flow. Flow rate measured at the outflow of the wetland ranged from 100-160 gpm from September 1986 to August 1987, but declined to 50-65 gpm in September 1987. Lower than normal precipitation in 1987 in combination with the site modifications of late August 1987 may have contributed to this flow reduction.

pH. Prior to wetland installation the pH on average decreased from 6.16 to 5.88 between the seep (DN01) and the final sample point (DN02; table 2). Following wetland installation the pH has remained relatively constant. Although too early to detect a pattern, following site modifications of August 1987 the pH of water leaving Cell 3 was the lowest (5.99) since wetland installation.

Iron. Total iron at the seep ranged from 80-241 mg/L from 1983-1987, but was usually 100-120 mg/L (table 3). Pre- and post-wetland iron levels can be compared at the end of the 100 m-long ditch below the wetland (station DN02, approximately 100-m below the pond outlet) which was sampled prior to and after wetland installation. "Efficiency" (or more properly the percent reduction in iron concentration of effluent water relative to influent water) in removing iron is defined as:

$$\frac{\text{Total Fe conc. at DN01} - \text{Total Fe conc. at DN02}}{\text{Total Fe conc. at DN01}}$$

Table 2.--Average pH values by season of each wetland cell and ditch outfall; N=5 for pre-wetland means, N=4-7 for post-wetland means.

Location	Pre-wetland (1983-1985)	Winter 1985-6	Spring 1986	Summer 1986
Seep	6.16	6.45	6.40	6.40
Cell 1	--	6.07	6.52	6.40
Cell 2	--	5.92	6.46	6.22
Cell 3	--	6.03	6.40	6.22
Ditch End	5.88	6.07	6.50	6.24

	Fall 1986	Winter 1986-7	Spring 1987	Summer 1987	Fall 1987*
Seep	6.46	6.34	6.25	6.36	6.39
Cell 1	6.16	6.48	6.45	6.33	6.29
Cell 2	6.16	6.48	6.40	6.31	6.27
Cell 3	6.47	6.36	6.27	6.19	5.99
Ditch End	6.16	6.50	6.43	6.26	6.18

* after site modifications of August 31, 1987

Winter = Dec-Feb
Spring = Mar-May
Summer = Jun-Aug
Fall = Sep-Nov

Prior to wetland installation the total iron concentration was reduced by an average of 32% between DN01 and DN02 (180-122/180). During the first winter following installation the iron reduction efficiency for the wetland (at DN02) was 35% (table 4). This efficiency rose through the spring and summer to 81% in July 1986, averaging 75% in its first summer and 70% in the second summer. The efficiency in the second winter (1986-7) exceeded that of the first winter, 53% to 35%, as did the efficiency of the second spring to the first, 62% to 47%. Using this efficiency index, this wetland is improving over time (fig. 3).

Because station DN02 is 100-m below the wetland, a more accurate gauging point for wetland efficiency is ES03, which is at the outfall of the third (final) wetland cell. The efficiency at ES03 reflects the effect of the wetland system proper on water quality. The cumulative percent reduction at ES03 (table 4) climbed steadily from 28% to 56% in the summer of 1986 and remained near that level until the following summer, when it rose to 62%. Thus, (a) there was not a significant dropoff in the wetland's efficiency in the reduction of iron over the winter, and (b) the level of iron

Table 3.--Average total iron (mg/L) by season of each wetland cell and ditch outfall; N=5 for pre-wetland means, N=4-7 for post-wetland means.

Location	Pre-Wetland (1983-1985)	Winter 1985-6	Spring 1986	Summer 1986
Seep	180 (range:144-241)	116	106	127
Cell 1	---	99	93	98
Cell 2	---	93	81	77
Cell 3	---	84	65	56
Ditch End	122	75	55	32

	Fall 1986	Winter 1986-7	Spring 1987	Summer 1987	Fall 1987*
Seep	144	113	100	87	100
Cell 1	123	100	78	68	62
Cell 2	105	86	63	59	59
Cell 3	74	60	42	34	26
Ditch End	58	52	38	26	19

* after site modifications of August 31, 1987

Winter = Dec-Feb
Spring = Mar-May
Summer = Jun-Aug
Fall = Sep-Nov

Table 4.--Average percent reductions in total iron concentration by season of each wetland cell, the ditch, cumulative (cum.) for the wetland proper, and end of ditch; N=4-7 for each season.

Component	Winter 1985-6	Spring 1986	Summer 1986	Fall 1986
Cell 1	14	12	22	17
Cell 2	6	12	20	14
Cell 3	12	18	27	29
Ditch	10	16	42	22
Cum. wetland	28	37	56	53
Cum., end of ditch	35	47	75	59

Component	Winter 1986-7	Spring 1987	Summer 1987	Fall 1987*
Cell 1	17	21	22	38
Cell 2	15	17	17	41
Cell 3	30	33	42	56
Ditch	8	13	22	26
Cum. wetland	51	55	62	73
Cum., end of ditch	53	62	70	81

* after site modifications of August 31, 1987

Winter = Dec-Feb
Spring = Mar-May
Summer = Jun-Aug
Fall = Sep-Nov

reduction was much greater in the second winter (51%) than the first winter (28%). In the interval between the first and second winters this constructed wetland experienced its first growing season.

A knowledge of the efficiency of each wetland cell is valuable in further evaluating the wetland system. The percent reduction of Cell 1 is the efficiency up to ES01; the percent reduction of Cell 2 uses ES02 and ES01 as reference points; and the percent reduction of Cell 3 uses ES03 and ES02 as reference points. Prior to the site modifications, Cells 1 and 2 showed peak efficiencies in the summers of 1986 and 1987. The variation here is high, but 3-month summer averages for Cells 1 and 2 are 22% and 20%, respectively (table 4). The efficiencies for these two cells decreased slightly after the summer (3-month averages of 17% and 14%). Cell 3 efficiency, however, has increased steadily since installation, performing at twice the efficiency of Cell 2. The improvement of the wetland system proper from 28% (1986) to 51% (1987) in winter efficiency is in large part due to the high winter efficiency of Cell 3. The decline in cumulative efficiency at point DN02 in the fall and winter of 1986-7 is therefore not due to the action of the wetland itself, but to the decreased removal in the ditch between ES03 and DN02. Iron removal by the ditch ranged from a high of 42% in summer 1986 to only 8% in winter 1986-7 (table 4).

Water samples were taken within the wetland at each of 40 stations on a quarterly basis. Representative results for August 1987 (fig. 4) indicate that no sharp transition zones of iron reduction exist; a gradual decrease in iron content in the water occurs from inlet to outlet. Higher iron levels are present on the right-hand (highwall) side of the wetland; this is probably due in large part to the much greater flow and channeling observed on this side prior to the August 31, 1987 modifications.

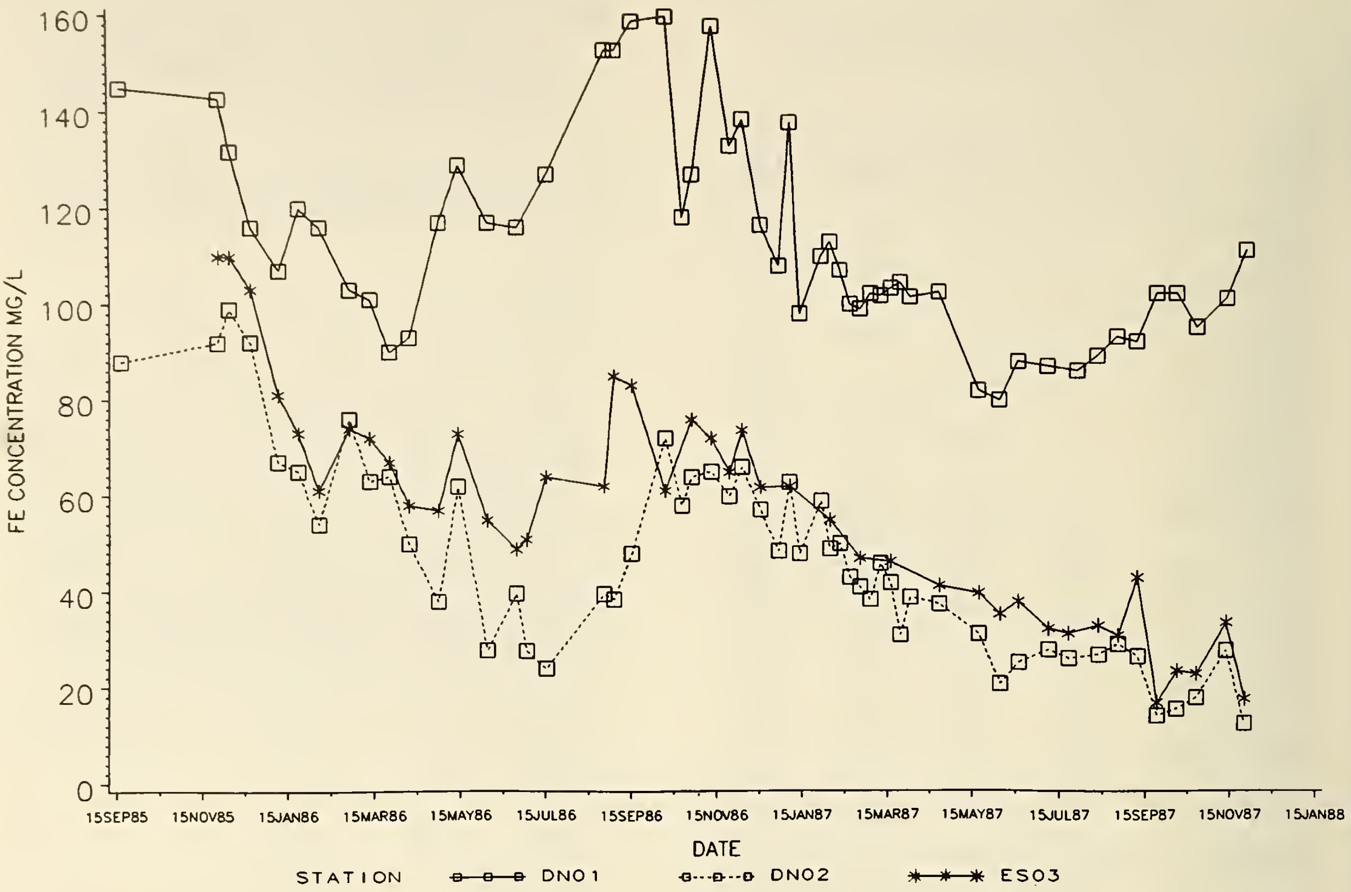

Figure 3.--Total iron concentrations at DNO1 (seep), ESO3 (wetland proper outlet), and DNO2 (100-m below wetland).

The introduction of hay bale dikes and the diversion of half the water around each of Cells 1 and 2 (performed between the summer and fall of 1987) resulted in a further reduction of iron in the water. Although we cannot predict how the wetland would have performed without modification, we can compare patterns between the summer-fall of 1986 and the summer-fall of 1987. In the fall of 1986 the cumulative percent reduction in the iron concentration after passing through the wetland was 53% (table 4), 3% lower than the summer 1986 efficiency. However, the iron reduction efficiency in the fall of 1987 was 73%, 11% higher than that of the preceding summer. Each wetland cell increased in efficiency (a direct increase of 14% to 24%; table 4), with the middle cell showing the most dramatic improvement. Prior to site modifications, summer had been the season of peak performance for iron reduction (56% and 62%). However, in the fall of 1987 after modification, an all-time seasonal high of 73% was recorded (table 4).

Manganese. Total manganese in the seep water ranged from 1.66-6.02 mg/L from 1983-1987, averaging 2.12 since 1985 (N=43). Wetland outlet water over the same period has ranged from 1.81-6.09 mg/L, averaging 2.28 mg/L (N=43). Thus, the Mn concentration in the water increased by 8% between seep and wetland outlet, with the elevation occurring in Cells 1 and 2. Although the manganese levels are a minor concern due to their low levels, the probable explanation of the slight elevation in Mn over the first two wetland cells was found to be a small surface side seep of <1 gpm alongside Cell 1 that contained about 5 mg/L Mn and negligible Fe.

Acidity. Pre-wetland acidity at the seep and the ditch outfall averaged 207 and 187 mg/L, respectively: an improvement of 10%. The effect of the wetland was to reduce acidity (table 5): from the summer of 1986 forward the wetland has lowered acidity by at least 63%. Cell 3 has been the most effective cell in reducing acidity in five of the seven seasons, followed by Cell 1.

Sulfate. No data on sulfates are available prior to wetland installation. Since late 1985, sulfates in the seep water have averaged 1,226 mg/L (N = 40; range = 964-1,841 mg/L). The wetland has lowered this level by 7%, (N = 40; range = 425-1,931 mg/L).

Vegetation

Following the initial Typha latifolia transplants the wetland has basically been allowed to establish on its own. Seventeen species of plants have appeared in the wetland, but only a few account for a significant biomass based on coverage (table 6): Typha latifolia, Leersia oryzoides, and mixed algal populations including primarily Oscillatoria sp., Chlamydomonas polypyrenoideum, and Euglena sp.

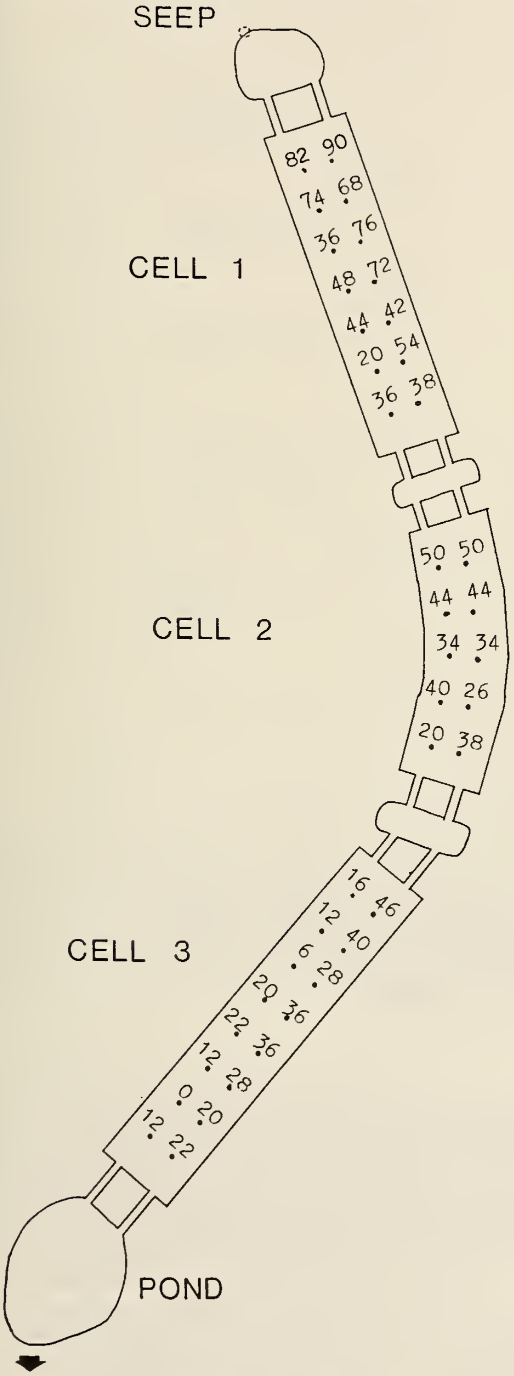

Figure 4.--Dissolved iron (mg/L) in water samples taken at 40 evenly spaced stations within the wetland, August 1987.

These three elements (i.e., the two higher plants and the algae) accounted for 87% of the total plant cover in 1986, and for 92% in 1987.

Total cover in 1986 was 45%; in 1987 it increased to 83%, in large part due to increased growth of the three elements above. The cutgrass (Leersia) was a relatively minor element of the vegetation in 1986, but in 1987 attained one-half the cover of the cattails. Cell 3 has the highest coverage of flowering plants, while Cell 2 cover increased dramatically in 1987. Algae were quite abundant in Cell 2, in part due to the frequent open spaces with reduced higher plant cover. The cattail cover in Cell 1 did not increase between 1986 and 1987; muskrats were present in this cell, fed on cattail rhizomes, and were trapped out intermittently.

Cattail shoot counts in August 1987 yielded the following estimates of shoot density per wetland cell (N is the number of 0.5-m^2 quadrats sampled): Cell 1: 6.5/m^2 (N=8); Cell 2: 12.0/m^2 (N=6); Cell 3: 18.7/m^2 (N=9). Clearly cattails are more numerous in Cell 3.

Table 5.--Average total acidity (mg/L) by season of each wetland cell and ditch outfall; parenthetical values are the percentage reduction in acidity from the seep; N=5 for pre-wetland means, N=4-7 for post-wetland means.

Location	Pre-Wetland (1983-1985)	Winter 1985-6	Spring 1986	Summer 1986
Seep	207	95	52	92
Cell 1	---	82	38	57
Cell 2	---	76	36	32
Cell 3	---	70	26	15
Ditch End	187 (10%)	65 (32%)	22 (58%)	1 (99%)

	Fall 1986	Winter 1986-7	Spring 1987	Summer 1987	Fall 1987*
Seep	88	54	57	46	61
Cell 1	64	38	25	24	3
Cell 2	59	27	22	15	17
Cell 3	41	20	14	3	-4
Ditch End	20 (77%)	20 (63%)	15 (74%)	6 (87%)	-3 (100%)

* after site modifications of August 31, 1987

Winter = Dec-Feb
Spring = Mar-May
Summer = Jun-Aug
Fall = Sep-Nov

Table 6.--Coverage of plant and algal species by cell in 1986 and 1987. A "--" denotes absent, and a "+" denotes present but with less than 1% mean cover.

Species	Cell 1		Cell 2		Cell 3		Overall	
	1986	1987	1986	1987	1986	1987	1986	1987
Typha latifolia (cattail)	29	28	20	48	39	51	30	42
Leersia oryzoides (cutgrass)	2	8	1	20	6	35	4	22
Lemna minor (duckweed)	--	--	6	2	7	5	4	2
Equisetum arvense (horsetail)	--	--	--	--	1	+	+	+
Phalaris arundinacea (reed canary grass)	1	6	--	--	--	--	+	2
Polygonum sagittatum (tear-thumb)	--	--	--	--	1	+	+	+
Verbena hastata (vervain)	--	--	--	--	+	--	+	--
Salix sp. (willow)	--	--	--	--	+	--	+	--
Alisma sp. (water plaintain)	--	+	--	2	--	--	--	1
Ailanthus altissima (tree of heaven)	--	+	--	--	--	--	--	+
Epilobium sp. (willow-herb)	--	--	--	2	--	1	--	1
Algae*	9	12	--	24	5	4	5	12
TOTAL	41	55	27	98	60	97	45	83

*-including: mixed populations of *Oscillatoria* sp.; 2 *Euglena* sp.; *Chlamydomonas polypyrenoideum*; and *Microspora pachyderma*.

In the winter, 22 of 40 quadrats had visible algal populations, with 12 of these in Cell 3. Overall algal cover in the spring was 41%, with Cell 1 = 54%, Cell 2 = 30%, and Cell 3 = 37%. The algae are a prominent vegetational element on the substrate and water surfaces year-round.

Plant Tissue Metal Levels

Cattail roots at the Simco #4 wetland had the highest iron concentrations, followed in sequence of decreasing concentrations by outer rhizomes, entire rhizomes, leaf bases, leaf blades, and inner rhizomes (table 7). Control plants had higher iron values in the outer rhizome samples than found in the experimental (i.e., Simco #4 wetland) plants. Control root values were greater than three of six experimental values. Although no apparent surface mining has occurred in the immediate watershed where controls were taken, it is possible that some past disturbance has resulted in elevated iron levels in the substrate.

All roots and outer rhizome samples were iron-red and had iron encrustations on the surface that were difficult to remove from the epidermis. Inner rhizome tissues and hand-sectioned root tissues were not discolored. These observations correlate with the higher iron values observed in this study. Taylor et al. (1984) demonstrated that iron coatings (plaques) form on the surface of

Table 7.--Average iron and manganese concentrations (mg/g dry weight) in plant structures of Typha latifolia from the Simco #4 wetland and a control site near DuBois, PA; numbers of plants sampled in parentheses.

Structure	Location (Cell No.)	Fe Jan '87	Fe Apr '87	Mn Jan '87	Mn Apr '87
Leaf Blade	1	--	0.86(2)	--	0.47(2)
	2	--	1.02(2)	--	0.41(2)
	3	--	1.27(3)	--	1.86(3)
	Control	0.65(3)		1.07(2)	
Leaf Base (sheath)	1	14.69(1)	0.78(2)	0.02(1)	0.23(2)
	2	15.50(1)	0.92(3)	0.38(1)	0.13(3)
	3	--	1.20(2)	--	0.52(2)
	Control	0.26(3)		0.92(3)	
Inner Rhizome	1	0.55(4)	0.84(4)	0.12(4)	0.13(4)
	2	0.29(3)	2.70(2)	0.05(3)	0.07(2)
	3	0.33(4)	1.52(5)	0.21(4)	0.18(5)
	Control	0.39(1)		0.24	
Outer Rhizome	1	8.34(3)	22.16(2)	0.31(3)	0.18(2)
	2	12.77(3)	7.95(3)	0.05(3)	0.09(3)
	3	11.52(2)	2.51(2)	0.12(2)	0.27(2)
	Control	14.51(2)		0.41	
Entire Rhizome	1	3.61(4)	7.71(4)	0.06(4)	0.13(4)
	2	6.03(4)	1.73(2)	0.03(4)	0.09(2)
	3	2.46(3)	6.24(2)	0.12(3)	0.15(2)
	Control	0.60(1)		0.48(1)	
Root	1	9.11(4)	27.82(3)	0.11(4)	0.26(3)
	2	21.95(3)	41.65(2)	0.08(3)	0.10(1)
	3	107.04(2)	12.63(1)	0.20(2)	0.61(1)
	Control	21.40(2)		0.65(2)	

cattail roots when ferrous iron is oxided and is deposited on the roots and in the adjacent rhizosphere. Macfie and Crowder (1987) found that iron plaque formation in cattails was positively correlated with extractable iron in the substrate and pH. Consequently, higher iron values would be expected in surface tissues than in inner tissues.

Roots and rhizomes have higher iron concentrations than foliar tissues (table 7). Other researchers have found the same pattern in cattails (Taylor and Crowder 1983; Adriano et al. 1984). In contrast, foliar samples of cattails had higher manganese concentrations than rhizome and root samples (table 7). Adriano et al. (1984) found no seasonal patterns for manganese accumulation. However, their study demonstrated rhizomes had much lower concentrations of manganese than shoots.

Microbial Studies

Respectably high numbers of aerobic heterotrophs (the average viable cell count for the entire wetland was 1.4×10^8 colony forming units/mL sediment) occurred in the wetland. Typical trends in the numbers of aerobic heterotrophs through the wetland from the seep to the outfall are shown in fig. 5. An obvious bloom in the total population of aerobic heterotrophs (averaging about two orders of magnitude in increased population) was seen in the spring samples. Bacterial numbers were lowest in the winter samples. The highest viable cell counts were found on agar-water and brain heart infusion agar. To put these results into context over a 1-year period, the numbers of bacteria in the wetland samples were about two orders of magnitude lower than those found in rich agricultural soils, about the same as those found in eutrophic lakes, and three orders of magnitude higher than those found in oligotrophic lakes. However, species diversity of the aerobic heterotrophs was variable and relatively low over the wetland, averaging only between 9 and 25 distinct colony types. Also, iron- and manganese-oxidizing bacteria were quite variable (from none detected to over 10^8/mL of sample) through the wetland (data not shown). This was surprising because the decline in soluble iron from the seep to the outfall was relatively smooth, while the manganese content increased slightly. Black water with the characteristic smell of H_2S and that of mercaptans was noted, especially in

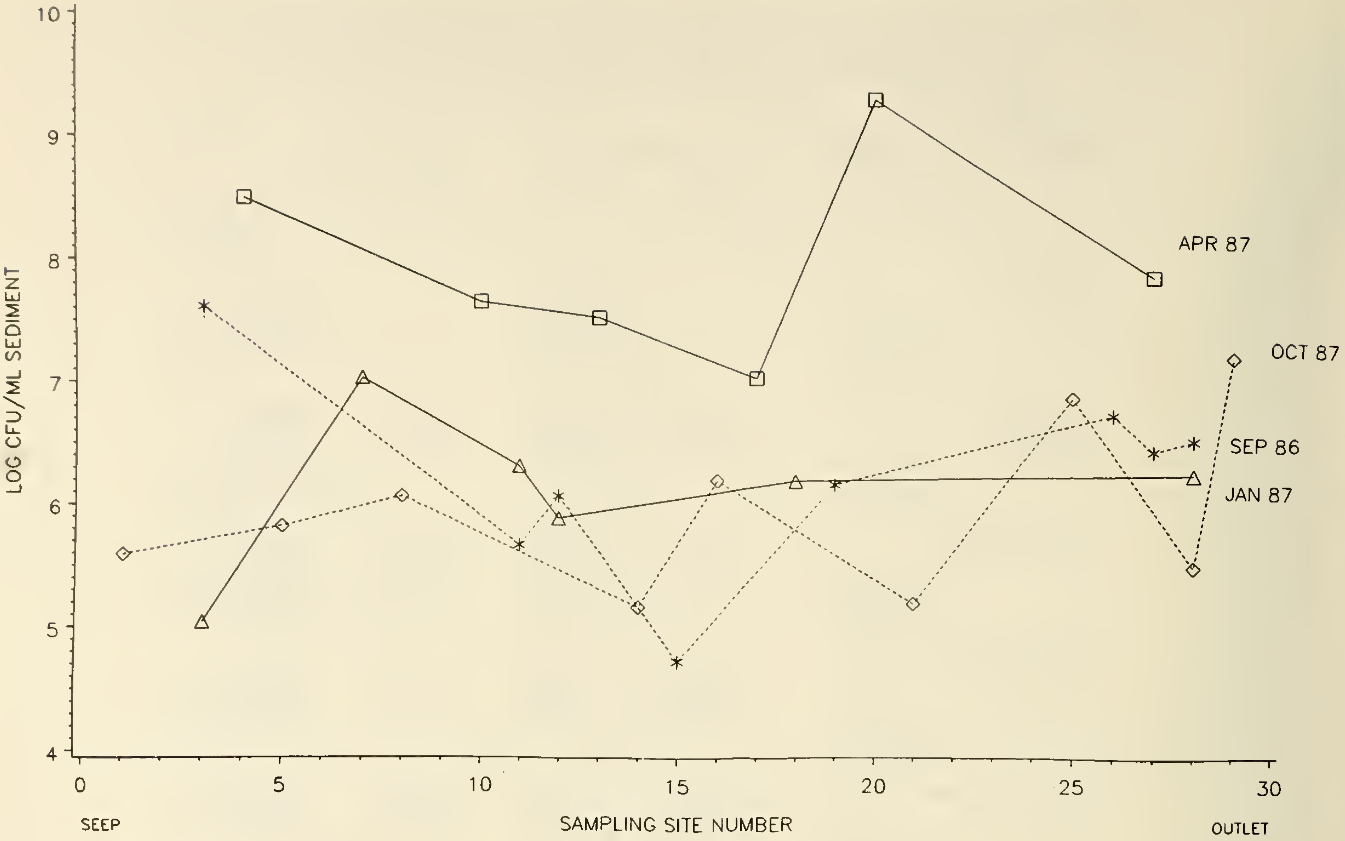

Figure 5.--Viable counts of microbes on agar water medium by location in the wetland expressed as the log of colony forming units per mL of sediment (CFU/mL). Sampling site 1 corresponds to the seep; 29 corresponds to the outlet.

association with bales of hay placed in the wetland to alleviate channelization.

DISCUSSION

Given the relatively high pH of this mine drainage, iron is expected to come out of solution to some degree and settle without the presence of a wetland. In addition, the elevated pH probably enhances the biological responses to metals at the cell surface (Campbell and Stokes 1985). Thus, the seep pH of 6.0, which is relatively unaltered by the wetland, positively influences the wetland with respect to iron. At this point, it is impossible to discriminate between the pH effect on iron solubility and the pH effect on biological surfaces and cation exchange. However, the effect of wetland installation on iron removal is significant: iron removal 2 years after wetland construction is up 80%-90% over pre-wetland iron removal. Why is this the case? There are a few conspicuous differences between pre- and post-wetland sites, and several wetland factors to consider regarding the wetland's apparent effectiveness:

(1) The area of water impoundment has been increased by wetland installation. As a result the amount of water exposed to the air is much greater.

(2) The retention time of the water was probably increased by wetland installation. Therefore, any biologically assisted or unassisted reactions leading to iron precipitation have a longer period in which to occur.

(3) Biological activity in the form of microbial, algal, and cattail-cutgrass populations is much greater following wetland construction and vegetation cover increased considerably from the first to the second summer. This activity was promoted principally by the addition of organically rich compost growth medium for the cattails. Cattails are highly productive and thereby return a considerable amount of organic material to the system via winter die-off of stems and leaves. Any effect of the substrate apart from biological activity cannot account for all of the iron removal. During the first winter (1985-6) following wetland construction little else but spent mushroom compost was in the wetland; the winter efficiency was 28%, approximating pre-wetland efficiency. However, during the second winter (1986-7) efficiency increased to 51%. This difference is probably attributable to biological activity.

(4) Cattail roots and rhizomes are directly absorbing or precipitating some of the iron. Roots from cattails at Simco #4 contained up to

5 times as much iron as cattail roots from a control site. Iron precipitates are also loosely associated with cattail roots and rhizomes. The cattail rhizosphere may be a conducive environment for aerobic microbes such as species of Thiobacillus that oxidize iron. Further study will determine whether the distribution of iron in the substrate of a wetland receiving mine drainage is related to proximity to roots.

(5) Wetland Cell 3 was the most effective portion of the constructed wetland in improving the water quality. It is the largest cell, but the degree of water improvement is greater than can be accounted by size difference. Other characteristics of Cell 3 include the highest total flowering plant cover, the greatest density of cattail stems, and cutgrass coverage exceeding the other two cells. Microbial populations were no greater in Cell 3 than in the other cells. Cell 3 receives water with the lowest level of iron, and thus its higher efficiency may, alternatively, reflect (a) a water pretreatment effect of previous cells, or (b) that iron is more easily removed by a wetland at lower incoming levels.

(6) The diversion ditches and hay bale dikes installed in the fall of 1987 had an immediate effect on iron removal (increased), pH (decreased), manganese (increased), and acidity (decreased). It is likely that hay, much like sawdust, encourages anaerobic sulphate-reducing bacteria that precipitate FeS - FeS_2 (Tuttle et al. 1969). On the downstream side of hay bales conspicuous areas of black water were observed, consistent with this hypothesis.

(7) The roles of algae in this wetland are not yet understood, but their ubiquitous presence, both in the floating iron surfactant/flocculant (primarily Oscillatoria) and at the substrate-water interface, deserves further study.

(8) Little is known about heterotrophic bacteria in acidic mine drainage. However, they have been shown to be involved in ferric iron reduction and in iron deposition in freshwater lakes (Jones 1986). Aerobic and facultatively anaerobic bacteria are thought to contribute to iron and possibly manganese removal primarily through reduction of these metallic species. Ferric iron could be reduced to iron oxide (FeOOH), which is believed to be the reactant with HS^- that leads through mackinawite to greigite and finally to pyrite (see Jones 1986 and references therein). The HS^- is produced anaerobically by several species of bacteria. Anaerobic bacteria have not yet been counted in the wetland, but as noted previously, the products of sulfate reduction by bacteria were obvious at each of the visits to the wetland. The oxidation of iron was evident in the wetland, as indicated by the deposition of $Fe(OH)_3$ and the formation of yellow-boy. This was especially evident around the shallow outlets and inlets of the seep and each cell. These areas were undoubtedly the most aerobic zones in the wetland. Iron-oxidizing bacteria of the genus Thiobacillus were found throughout the wetland.

(9) The winter efficiency of wetlands receiving mine drainage has frequently been questioned. Data from Simco #4 indicate only a slight reduction in iron-removal efficiency between summer and winter (56% to 51%). This result is encouraging, but the water quality and other site-specific conditions prohibit generalizations at this point.

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TREATMENT OF DISCHARGE FROM A HIGH ELEVATION METAL MINE IN THE COLORADO ROCKIES USING AN EXISTING WETLAND

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Abstract. During the summer of 1986, discharge from the Pennsylvania Mine was diverted into a natural sedge wetland in an experiment to assess the metal removal capability of a wetland type common to the higher elevations of the Rocky Mountains. The Pennsylvania Mine is an abandoned metal mine located at an elevation of 3355 m in the Peru Creek basin of Central Colorado. Surface discharge from the mine averages 380 L/min with a mean pH of 3.6 and average concentrations (in mg/L; n = 6) of the following metals: Fe, 50; Zn, 25; Mn, 20; Al, 15; Cu, 6; Sr, 0.7; Cd, 0.1; Ni, 0.1; and Pb, 0.1. During the course of the investigation it was determined that the wetland was heavily contaminated with metals prior to the experiment, apparently coming from metal-laden surface and colluvial waters. Soil metal concentrations (mg/kg; n = 12) averaged: 23,195 for Al; 100,899 for Fe; 159 for Mn; 3876 for Cu; 3713 for Zn; 3.17 for Ni; 42.2 for Cd; and 921 for Pb. Total soil metals *per se* was not correlated with the qualitative health of plants in the wetland, but high concentrations of copper, zinc, nickel and cadmium were associated with poor plant health. Because of the low hydraulic conductivity of the peat soils (10^{-3} to 10^{-4} cm/sec) the ability of the fen to accommodate drainage from the adit was limited and the experiment was terminated. However, the study demonstrated that the plant species present (mainly *Carex aquatilis*) have a high tolerance for metals and low pH and thus have good potential for use in constructed wetland treatment systems in the Rocky Mountains.

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[1] Paper presented at the annual meeting of the American Society for Surface Mining and Reclamation

INTRODUCTION

Mine drainage and leachate from mine spoil and mill tailings are serious water quality problems in some parts of Colorado. Eight Superfund sites are focused on the clean-up of wastes from decades of mining activity, and a recent study (Lewis et al. 1987) estimated that out of a total of 29,766 km (18,500 mi) of streams and rivers in the state, over 6200 km (3000 mi) have dissolved metal concentrations that exceed basic standards for aquatic life, agricultural use, or domestic water supply. Approximately 2,896 km (1,400 mi) of that mileage is considered to be a direct result of pollution from inactive mining operations. These problems have spawned an interest by Colorado agencies to investigate passive treatment methods for mine drainage abatement. While such methods commonly are used in coal mining regions of the eastern U.S., colder climates, rougher terrain, and greater amounts of heavy metals in the Rocky Mountain mineral belt have impeded direct transfer of this technology to many western areas.

This paper reports the results of one such investigation conducted during the summer and fall of 1986 when a natural high-elevation wetland was used in an attempt to treat discharge from an inactive mine.

While the treatment attempt met with poor success, the project provided an opportunity to assess metal accumulation in soils and native plants, and tolerance of the plants to high metal concentrations. Biological and geochemical processes that are responsible for metal retention in mountain wetlands are poorly documented. The work described here is being conducted with the aim of increasing the knowledge of these processes, thus leading to the development of criteria for the feasibility and design of constructed wetlands to treat mine drainage at high elevations in the Rocky Mountains.

SITE DESCRIPTION

The Pennsylvania Mine, located at an elevation of 3355 m (11,000 ft) near Peru Creek in the Front Range of central Colorado, is an inactive gold and silver mine with thousands of meters and many levels of underground workings. Surface discharge from the mine averages 380 L/min with a mean pH of 3.6 and mean concentrations (in mg/L; n = 6) of the following metals: Fe, 50; Zn, 25; Mn, 20; Al, 15; Cu, 6; Sr, 0.7; Cd, 0.1; Ni, 0.1; and Pb, 0.1. The mine drainage seriously impacts Peru Creek, and in many ways is typical of mine drainage problems in the Colorado mineral belt. Prior to this study, the discharge from the Pennsylvania mine flowed in a ditch from the adit to Peru Creek, dropping approximately 25 m over a distance of 150 m.

During a portion of this study, mine drainage was diverted into a 1.6 ha wetland located approximately 180 m from the mine and a few meters above the Peru Creek channel. The wetland is technically a fen, since it is underlain by highly organic soils and is receiving nutrients and water from sources other than precipitation (Daubenmire, 1968). It is dominated by a near monoculture of water sedge (Carex aquatilis) interspersed with patches of bog birch (Betula glandulosa) growing on many of the larger hummocks. The soil surface is covered by 1 to 5 cm of water over much of the wetland throughout the growing season. Soils are characterized by accumulations of peat to depths of up to 2 m. The upper 10 cm of soil averages 41 percent organic matter, with the texture of the inorganic fraction typically loam or clay loam. Over much of the wetland the upper 3-4 cm of soil are oxidized and are characterized by reddish iron oxyhydroxides, and below this depth the soil consists of gray to black reduced sediments with an occasional strong smell of hydrogen sulfide. Ruins of several mine buildings including a small mill are located just above the wetland, and mill tailings cover the surface of the western third of the wetland. The majority of plant and soil samples taken for characterization of "natural" conditions were from the eastern half of the wetland where impacts from mining activities appeared to be minimal. However, several shallow wells augured into the soil in that portion of the wetland indicated lenses of buried sandy material that might have been mill tailings.

DESCRIPTION OF THE STUDY

A mine drainage diversion system was constructed by the Colorado Division of Mined Land Reclamation during the fall of 1985. This system consisted of a PVC pipe that carried the mine water from the adit to a 150 m perforated leach line, which was buried at a depth of 1.5 m along the upper margin of the wetland. In addition, ten 5-cm diameter wells were installed in the organic soil layer of the wetland to monitor metal concentrations in the interstitial water. The wells were grouped into three parallel transects approximately 30 m apart and roughly perpendicular to the expected flow of water through the wetland. The upper transect closest to the leach line was comprised of three wells, the middle transect consisted of four wells, and the remaining three wells were in the lower transect.

A sampling program was carried out during the summer and fall of 1986 and 1987 to monitor metals in Peru Creek and interstitial water in the wetland, as well as metal concentrations in soils and plants. This paper summarizes some of the results of that sampling program, chiefly from the well transects mentioned above, and from six intensive study sites in the wetland where metals in soils and plants were monitored. The leach line system was activated from August 25, 1986, to October 29, 1986. Three series of water samples were collected from the wetland wells prior to the diversion of mine water, and one series was collected 30 days following diversion. During 1987, metal sampling continued in soils and plants, although the leach line system was not reactivated.

All water and soil samples were analyzed by the Colorado State University Soil Testing Laboratory. Water samples were analyzed by inductively coupled plasma emission spectrometry (ICP). Soil metals were determined by nitric-perchloric acid digestion followed by ICP analysis, and cation exchange capacities were measured by displacement using ammonium chloride as the saturating salt, using methods based on Page et al (1982). Metals in plant samples were extracted with sulfuric acid and then analyzed by ICP.

RESULTS

Diversion of Mine Drainage

Introduction of the mine drainage into the wetland via the leach line system was partially successful. Average concentrations of several metals in the upper transect of ground water monitoring wells were significantly higher than before the system was activated (Table 1), indicating percolation of mine drainage into the wetland. However, the relatively low hydraulic conductivity of the peat soils (calculated using Darcy's law to be in the range of 10^{-3} to 10^{-4} cm/sec) did not permit the entire flow from the adit to pass into the wetland, nor did the seepage from the leach line appear to pass beyond the upper well transect. The average metal concentrations in the two lower well transects did not significantly change from the time the system was activated until it was turned off and monitoring was terminated for the winter. While the diversion system was in operation, excess mine drainage that could not be accommodated by the peat soils leaked to the ground surface near the leach line and had to be routed around the wetland with a small interception ditch. The diversion system was not reactivated during 1987.

Metals in Plants and Soils

A preliminary survey of the wetland indicated that while the herbaceous cover consisted almost entirely of one sedge species (*Carex aquatilis*), plant growth and health was not uniform. More intensive vegetation measurements indicated a range in cover from 5 to 56 percent, and peak season standing crops ranging from 18 to 721 g/m^2 (oven-dried weight) of aboveground biomass. Areas of low cover and biomass were characterized by spindly, chlorotic plants, whereas sites of high cover and biomass typically had large, robust, green plants.

Surface water samples collected prior to activation of the leach line contained metal concentrations that, for some elements, mirrored concentrations found in the mine discharge. Table 2 shows data for five sites on the wetland, and illustrates that poor health was not necessarily associated with higher metal concentrations. Sites of poor health were usually found in areas that were poorly drained or in depressions between hummocks.

Mean concentrations of metals in soils and in sedge leaves are shown in Table 3. *Carex aquatilis* apparently is able to tolerate high concentrations of aluminum and iron,

Table 1. Mean metal concentrations (mg/L) in groundwater wells before and after diversion of mine water.

	Al	Fe	Mn	Cu	Zn	Ni	Cd	Pb
Upper Transect (3 Wells)								
Before (n=9	11.85	0.61	6.45	1.55	7.22	0.06	0.04	0.07
S.D.:	1.02	0.79	1.35	0.17	0.73	0.01	0.01	0.02
After (n=3)	23.03*	2.33*	9.44	1.58	13.67*	0.10*	0.08*	0.11*
S.D.:	2.64	1.37	6.14	1.13	2.15	0.01	0.01	0.00
Middle Transect (4 Wells)								
Before (n=12	3.70	12.56	5.23	0.02	0.94	0.03	0.01	0.06
S.D.:	3.76	11.13	2.37	0.01	1.42	0.02	0.00	0.02
After (n=4)	4.53	16.10	4.97	0.05#	0.86	0.33	0.01	0.09
S.D.:	5.86	2.45	2.40	0.04	1.11	0.03	0.00	0.08
Lower Transect (3 Wells)								
Before (n=9)	16.28	5.92	9.17	0.10	8.55	0.08	0.05	0.12
S.D.:	17.79	5.31	4.80	0.15	9.44	0.05	0.06	0.13
After (n=3)	11.80	9.13	7.14	0.03	4.36	0.06	0.01	0.15
S.D.:	9.64	4.44	3.46	0.03	5.83	0.04	0.00	0.12

Note: (*) significant increase at 99% confidence level
(#) significant increase at 95% confidence level
S.D. is standard deviation

Table 2. Metal concentrations and pH of five surface water samples collected from the Pennsylvania mine wetland on July 23, 1986, with corresponding plant cover and biomass measured at the sample locations.

Plants			Metals (mg/L)								pH
% Cover	g/m²	Health	Al	Fe	Mn	Cu	Zn	Ni	Cd	Pb	
8.4	109.9	P	16.4	13.0	2.44	1.74	0.10	0.02	0.01	0.05	3.3
8.8	42.6	P	14.0	0.13	10.3	1.88	10.9	0.07	0.07	0.06	3.6
18.0	68.3	I	15.7	0.22	12.4	1.70	13.9	0.09	0.07	0.09	3.2
28.0	492.0	I-R	12.6	0.56	8.81	2.23	11.2	0.07	0.10	0.05	3.6
44.0	536.0	I-R	12.7	0.50	8.11	2.00	8.55	0.06	0.06	0.06	3.8

Note: P denotes poor, I denotes intermediate, and R denotes robust

Table 3. Mean concentrations of metals (mg/kg) from samples of soils and *Carex aquatilis* leaves collected during the summer of 1987 (n = 2 for each site).

Plant Health	Al	Fe	Mn	Cu	Zn	Ni	Cd	Pb
				SOILS				
Poor (2 sites)								
	14285	6323	143	8298	10228	9.5	119.8	1037
S.D.:	4035	3900	17.9	1953	3392	2.9	66.0	855
Intermediate (3 sites)								
	26517	178167	195	2017	370	<1	4.0	750
S.D.:	6222	58687	31.9	1544	176	0.0	1.8	126
Robust (1 site)								
	31050	58250	85	612	717	<1	3.0	1201
S.D.:	3950	37850	25	395	199	0.0	0.0	171
				PLANTS				
Poor								
	92.8	372	696	30.1	351	5.0	0.75	5.3
S.D.:	23.3	243	26	3.3	77	1.2	0.25	0.4
Intermediate								
	114.8	516	621	80.7	427	9.5	1.27	<5
S.D.:	40.7	134	70	26.8	78	1.5	0.47	0.0
Robust								
	52.5	160	314	28.5	257	3.5	0.80	6.0
S.D.:	3.5	33	38	5.5	13	0.5	0.20	1.0

Note: S.D. is standard deviation

and under the conditions observed so far at the wetland, we have seen no significant correlation between amounts of these metals in the soils and corresponding plant health. However, high copper concentrations in the soil frequently is associated with poor growth, and to a lesser extent zinc, cadmium, and nickel have shown a similar trend. The highest values of these metals were always associated with sites of poor health, while the lowest concentrations were found on the healthiest sites. We observed no correlation between plant growth and total soil metals, even when total metal concentrations at some sites exceeded 300,000 mg/kg.

An important growth factor is the nutrient status of the plants. Metals can inhibit nutrient uptake and metabolism, causing nutrient deficiency symptoms, and mountain soils are often low in certain nutrients (Johnson and Cline, 1965). We examined soil calcium, nitrogen, phosphorus, and potassium, and found that of these four nutrients, only soil potassium concentrations showed a significant correlation with plant cover (Figure 1).

Organic matter in the soils ranged from 5.8 percent to 79.1 percent, with mean percentages of 59.7, 35.8, and 16.5 for the poor, intermediate, and robust sites, respectively. Cation exchange capacities (CEC) were relatively low, with a range of 3 to 24 meq/100g, and a mean of 12.7. As would be expected, CEC values appeared to be closely related to the organic matter content of the soils. Metals extracted (displaced) during the CEC determinations of the soil samples represented from 1 to 12 percent of the total metals in the samples.

DISCUSSION AND CONCLUSIONS

Results of the mine drainage diversion study were inconclusive. The system was not in operation for a long enough period of time to permit percolation of the mine water completely through the wetland. However, given the relatively high pre-existing metal concentrations in the groundwater and soils of the wetland, it is questionable whether the system would have had much of a beneficial impact on water quality.

Analyses of the plants, soils, and surface and subsurface waters subsequently have verified that metal concentrations throughout the wetland are high. The source of the metals is apparently from surface and colluvial waters flowing from the slope above the wetland, probably passing through a portion of the waste rock dump of the mine. Because of the relatively thick peat accumulations, the age of the wetland is probably several thousand years old, and it is possible that it was receiving metals before mining activities began nearly a hundred years ago. We have been conducting studies on other wetlands in this portion of the Colorado mineral belt and have found several sites that are receiving high metal loads of natural origin.

High metals concentrations _per se_ do not seem to limit the growth of _Carex aquatilis_ in the wetland. However, poor growth, characterized by low cover and biomass, spindly shoots, and chlorotic leaves appears to be associated with high soil concentrations of copper, zinc, nickel, and cadmium, as well as with low potassium concentrations. Perhaps the most significant factor adversely affecting plant health is poor drainage, judging from visual observations at the site. The healthiest plants generally are living on microtopographically high spots or on slopes where drainage is obviously better. These sites are also associated with lower percentages of soil organic matter. It is also possible that greater amounts of soil organic matter on sites of poorer health contribute to the formation of metal-organic complexes that may increase the availability of some metal species to the plants (Thornton, 1986). Clearly, the uptake of metals by _Carex aquatilis_ and the factors leading to toxic effects are complex issues that will require a more detailed study than was possible here.

It is apparent that _Carex aquatilis_ is tolerant of high metal concentrations and low pH and thus would be a likely candidate for use as a plant species in wetlands constructed at high elevations. Success of transplanting and rates of establishment remain to be determined for this species.

Metal absorption and retention by the soils from cation exchange appears to be relatively low and less important than other processes. Microbial uptake has not been studied at this site but presumably would play a role in metal retention by the wetland (Tuttle et al, 1969). Given the cold climate and relatively short growing season at mountain sites such as the Pennsylvania mine, it is likely that many of the biogeochemical processes that are responsible for metal accumulation in wetlands would be slower than at lower elevations. While this study has provided some insight into metal accumulation at one high-elevation wetland, a much greater research effort is needed before the feasibility of using a constructed wetland approach in such locations can be determined.

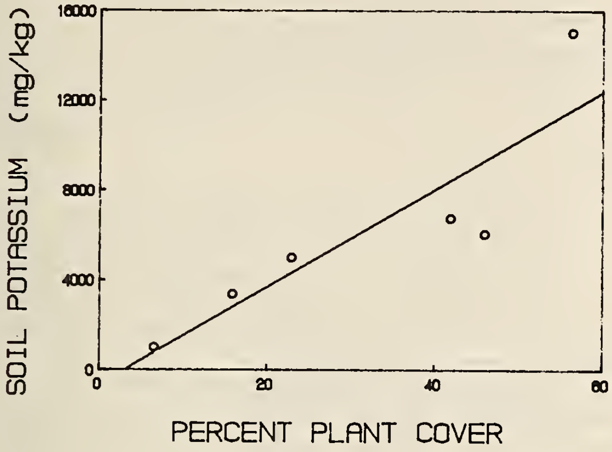

Figure 1. The relationship between soil potassium concentrations and percentage of plant cover on the Pennsylvania Mine wetland.

ACKNOWLEDGMENTS

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THE TRACY WETLANDS: A CASE STUDY OF TWO PASSIVE MINE DRAINAGE TREATMENT SYSTEMS IN MONTANA

Michael T. Hiel and Francis J. Kerins, Jr.[1]

Abstract.--Two man-made wetland systems were constructed in Montana to experiment with and assess applicability of Passive Mine Drainage Treatment technologies to the state. The wetland systems, designated the Large Tracy Wetland and the Small Tracy Wetland treat flows of .95 and .15 liters per second, respectively. Both wetlands were constructed during the summer of 1986 and utilize a peat substrate planted predominantly with Typha latifolia for metals removal and limestone gravel and aeration structures for pH buffering. The large wetland has approximately 418 square meters of surface area. The inflow to this system has metals concentrations in excess of 280 mg/L Al and 1.5 mg/L Mn. The small wetland has approximately 111 square meters of surface area. The inflow to this system has metals concentrations in excess of 143 mg/L Fe, 46 mg/L Al and mg/L Mn. Construction costs for the Large and Small Wetland were $67/m^2 and $140/m^2, respectively. Both wetlands were relatively ineffective in improving the water quality of the acid mine drainage. Low system retention times and minimal contact between the peat and acid mine drainage are primary reasons for the ineffectiveness of the systems.

INTRODUCTION

The Abandoned Mine Reclamation (AMR) Bureau of the Montana Department of State Lands (DSL) has identified more than 50 sites in Montana where acid mine drainage from abandoned mining facilities has significantly impacted the local environment. Passive mine drainage treatment techniques provide a potentially useful and economical means for mitigation of acid mine drainage impacts at many of these sites.

Two man-made wetland treatment systems were designed and constructed in Montana to treat acid mine drainage from abandoned coal mines. These wetlands, designated the Large Tracy Wetlands and the Small Tracy Wetlands, are located near the town of Tracy in the Sand Coulee drainage ten miles southeast of Great Falls in Cascade County. The wetlands were constructed during July and August of 1986.

This report presents design criteria and construction costs for both wetland systems. In addition, inflow and outflow water quality data, soil chemistry data, and plant tissue chemistry data are presented.

SITE DESCRIPTION

The Large Wetland treats a flow of .50 to .95 liters per second (11,520 to 22,000 gpd). This flow has a pH of 2.7, and total iron, total aluminum, total manganese, and sulfate concentrations of 284 mg/L, 178 mg/L, 1.51 mg/L and 2618 mg/L, respectively.

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The Large Wetland system includes a peat layer planted with cattails and sedges for metals removal, a limestone gravel channel for the neutralization of mineral acidity, and several aeration structures. A limestone-soil mix was used as a substrate throughout the system and in the construction of baffles to provide sinuosity.

The Small Wetland treats a flow of .38 to .50 liters per second (8,500 to 12,000 gpd). This flow has a pH of 3.1, and total iron, total aluminum, total manganese and sulfate concentrations of 148 mg/L, 46.7 mg/L, 1.2 mg/L, and 1560 mg/L, respectively.

The Small Wetland includes a peat layer, a limestone gravel channel, aeration structures, and a limestone-soil substrate. This wetland was also planted with cattails and sedges.

SITE LOCATION, HISTORY AND HYDROLOGY

The Great Falls area is a semiarid environment with a total precipitation of 38 cm (15 inches) per year. Seventy percent (70%) of the annual precipitation occurs during the months of April through September. The annual mean temperature is 7.2°C (45°F), with extremes from 37.8°C to -31.7°C (100°F to -25°F). Temperature and rainfall have a significant effect upon hydrology and soil characteristics.

The Sand Coulee drainage, consisting of approximately 500 sq. km (195 sq. mi.) in the upper Missouri River basin, is adversely impacted by acid mine drainage (AMD) from 22 discharging abandoned coal mines. This is the largest concentration of abandoned discharging coal mines west of the Mississippi River. Approximately 230 sq. km (90 sq. mi.) of the drainage contains abandoned coal mines discharging acid mine water.

The coal in this area occurs within the upper part of the Mission Formation (Jurassic) and is exposed along outcrops in the valley of Sand Coulee Creek and its tributaries. The topography is gentle with the exception of drainages incised into the plateau leaving a dissected and irregular terrain above the drainage areas. The Sand Coulee drainage lies in the Great Falls-Lewistown Coal Field, which is a large deposit of sub-bituminous coal. Unlike Eastern Montana Tertiary coal deposits, the coal in this area is higher in grade (11,118 btu/lb), and higher in sulfur content (0.5 - 5.5%) (Silverman and Harris, 1967). Thickness of the coal seam varies from .3 m to 3.6 m (one to twelve feet).

This coal was the target of the mining activity beginning in the 1880's. The last large-scale mine closed in 1952. During the period from 1885 to 1955 the coal mined from the Great Falls-Lewistown Coal Field exceeded 36 million tons. This amounted to about 23 percent of the total coal produced in Montana during that period. Coal mined from the Great Falls-Lewistown area from 1955 to 1965 was less than 1 percent of the total coal produced in Montana and since 1965 there has been no commercial coal production (Westech/Hydrometrics, 1982).

The geology of the area consists primarily of Cretaceous, Jurassic and Mississippian sedimentary rocks; the coal occurs in the Jurassic rocks. The Cretaceous Kootenai Sandstone and Flood Sandstone are aquifers most consistently used for water for domestic wells and springs in the area. Water from these aquifers leaks into the abandoned mines in the underlying formations.

The presence of large, abandoned underground coal mines in the area has apparently produced a large change in the regional ground water flow system. The underdraining of the basal Kootenai Sandstone aquifer by the abandoned mines has diverted the ground water flow, which most likely discharged to the Sand Coulee drainage prior to mining (Osborne, 1987).

The two mine discharges dealt with in this project are from the old Pierce Mine. Although a relatively small mine, the mine discharges have had a significant impact on the adjacent agricultural lands. For 40 years the discharges had been flowing into prime bottom land rendering .08 to .12 sq. km (20 to 30 acres) unsuitable for agricultural purposes. The problem persisted until even after several attempts by the landowner to seal the mine opening and reroute the flow of the discharge. In the fall of 1984, the Montana Abandoned Mine Reclamation Bureau (AMRB) completed a project which installed a drainage pipeline system. This pipeline collected drainage from both mines into a main pipeline and discharged directly into Sand Coulee Creek. Subsequent to the wheat field drying out, the soils have been amended and a wheat crop is once again growing. In solving the problem of flooding of the fields with acid mine drainage no attempt was made to treat the problem of acid mine drainage until this project in 1986.

WETLAND DESIGN

The sites chosen for construction of the experimental wetlands offered several advantages, including:

1. Two different controlled flows of less than one liter per second in proximity to each other;

2. Two flows having different pH's and metal concentrations;

3. Easy access to the sites during all seasons; and

4. A topography at the sites which provided some freedom in the design of the wetlands.

The larger flow where the Large Wetland was constructed has been monitored since 1970. The smaller flow where the Small Wetland was constructed has been monitored since 1986.

Design criteria for the wetlands were established following communication with people involved in the construction of similar systems in other states and a review of literature concerning wetlands construction techniques. The principal sources of information were the Colorado Inactive Mine Land Program (Holm, 1986) and a set of notes prepared by Kleinmann et al. (1986) for a course entitled, "Constructing Wetlands for the Treatment of Mine Water."

The intent of the wetland design was to provide a three-stage treatment facility: man-made peat wetlands planted with cattails and sedges, limestone-filled drainage channels, and aeration structures. The peat wetland planted with cattails and sedges provides an ion exchange facility for the removal of heavy metals. The limestone-filled channel provides a source of alkalinity for neutralization of the low pH drainage. The aeration structures provide a means for the exsolution of carbon dioxide to the atmosphere thereby reducing the concentration of carbonic acid (Guertin et al., 1985).

The primary criteria used for the design of the wetlands included:

1. Sizing the wetland to allow for treatment of the quantity of water expected during all seasons and following precipitation events. A surface area of 294 $m^2/L/s$ (200 ft^2/gpm) was considered a minimum size (Kleinmann, 1986).

2. Minimizing water velocities and maximizing retention time in the system.

3. Providing water depths varying from 5 cm to 46 cm (2 in. to 18 in.) in the system.

4. Providing optimum wetlands soils for emergent hydrophytes (such as Typha) composed of decomposed organic matter (peat) with some mineral soil content. The minimum depth of the peat was .3m (1 ft.).

5. Avoiding "short-circuiting" of the wetland by the formation of flow channels.

6. Providing for placing cattail sod mats over approximately 40 percent of the surface area of the wetlands.

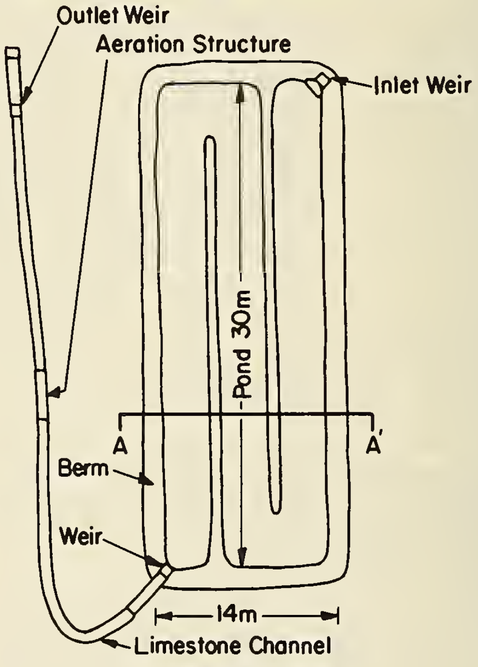
7. Providing a crushed limestone-filled channel downstream of the wetland for moderation of pH.

8. Providing aeration structures along the limestone channel.

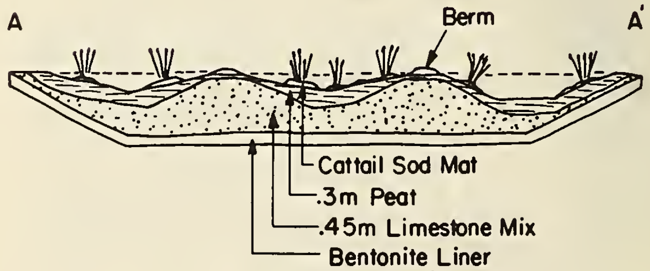
DESCRIPTION AND CONSTRUCTION

The Large Wetland was designed as a rectangular impoundment with the approximate dimensions of 30 meters (100 ft.) by 14 meters (45 ft.) (Figure 1). This impoundment was baffled by a berm extending 28 meters (93 ft.)

Figure 1—Large Wetland



PLAN VIEW



SECTION A–A'

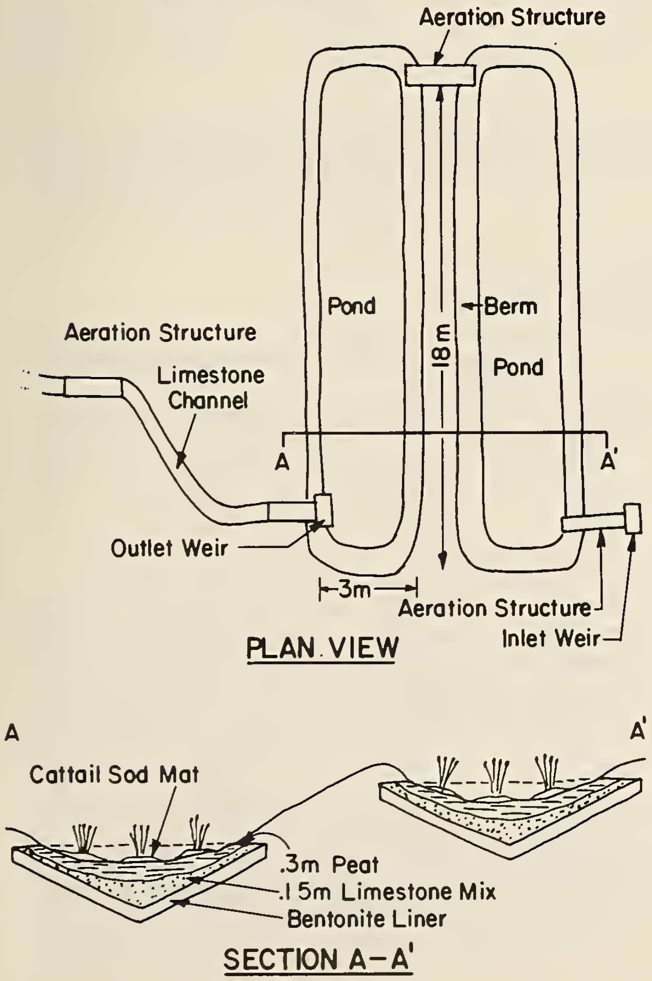
along the length of the wetland from each side of the wetland. This baffling provided sinuosity for the flow through the wetlands and prevented short-circuiting of the flow across the wetlands.

The water level is controlled by a rectangular notch weir at the outlet. The flow from this outlet structure passed over 37 linear meters (124 l.f.) of limestone channel and three aeration structures before exiting the system. Each of the aeration structures had about .45 meters (1.5 ft.) of fall.

The Small Wetland was designed as two parallel linear impoundments connected at one end by an aeration structure, forming essentially a U-shaped wetland (Figure 2). Each of the impoundments is about 18 meters (60 ft.) long and 3 meters (10 ft.) wide. The flow from the outlet structure passed over approximately 12 linear meters (40 l.f.) of limestone channel and two aeration structures before exiting the system.

The soil underlying both wetlands was amended with bentonite to prevent infiltration of the water in the impoundments into the ground. The base of both wetlands and the berms used for baffling in the Large Wetland were made of a limestone-soil mix with a minimum depth of .45 meters (1.5 ft.). A minimum of .3 meters (1 ft.) of peat was placed over the base material. The peat was from an active peat extraction operation located approximately 400 kms (250 miles) southwest of the project site. The species of moss, Polytrichum piliferum and Polytrichum strictum are common to Montana wetland communities and are more often found in drier locations. Cattail sod mats measuring approximately 3.3 sq. meters (36 sq. ft.) were placed on top of the peat, spaced evenly over approximately 40 percent of the area of the wetland. Sedge mats measuring approximately .09 sq. meters (.3 sq. ft.) were placed randomly throughout the wetlands.

Figure 2— Small Wetland



The cattail and sedge vegetation sod mats were excavated from a wetland source area about 250 meters (835 ft.) from the constructed wetlands. The mats were excavated using a rubber-tired front end loader. The average thickness of these mats was about 15 cm. (.5 ft.). Whole 2.7 meter by 1.2 meter (9 ft. by 4 ft.) mats were placed in the wetlands.

In order to minimize the stress on the transplanted vegetation uncontaminated water was used to partially fill the wetlands prior to inundation with mine drainage. The transplanted vegetation was allowed to adjust to the new environment for one week prior to coming in contact with mine drainage. It is believed that his procedure helps account for the significant "new shoot" growth shown after transplanting the Typha. No plant stress has been observed, and plant growth has been vigorous.

MONITORING

Influent and effluent water quality; metals concentrations in Typha roots, rhizomes and leaves; and metals concentrations in the peat for both systems have been monitored since the end of July 1986. Initially, water sampling was performed on a biweekly basis, but after the first two months a monthly sampling program was adopted. Vegetation and peat sampling was performed on a monthly basis.

Two water samples were collected at the inlet and outlet of each wetland. One of the samples taken from each location was filtered and preserved with acid (HNO_3). The pair of samples from each location was analyzed for total and dissolved aluminum, iron and manganese. The sulfate concentrations, pH, and specific conductance for each pair of samples was also determined. The samples were analyzed utilizing EPA drinking water methods and ICP (Inductively Coupled Argon Plasma) techniques.

The Typha rhizome, root and leaf samples were collected from randomly selected plants in the wetlands. After collecting the samples the rhizomes and roots were dried and any residual peat was carefully removed. Each of the vegetative samples was analyzed for total aluminum, iron, manganese and sulfur. The samples were processed using nitric acid and hydrogen peroxide digestion (EPA method 3050). Analysis of the samples utilized ICP techniques.

The peat samples were collected at locations near the inlet and outlet of each wetland. The samples were collected from the upper 15 cm (.5 ft.) of the peat layer. The samples were analyzed for a number of constituents, including total sulfur, pH and total and extracted iron, aluminum, and manganese. The samples were analyzed utilizing Montana Department of State Lands strip mining soil analysis methods.

PERFORMANCE

Neither the Large Wetland nor the Small Wetland has improved the quality of the water flow through the system to any degree. Table 1 shows a summary of the water quality data for the inlet and outlet of each of the wetlands.

The concentrations of iron, aluminum, and manganese in the rhizomes, roots and leaves of the cattail plants in the two wetlands and the cattail source area used as a control are summarized in Table 2. This data indicates that the *Typha* is concentrating metals in the system. However, because the potential uptake of metals by *Typha* is not significant when compared with the actual loading of the system, the vegetation

TABLE 1
Water Quality Summary

	Large Wetland				Small Wetland			
	Inlet		Outlet		Inlet		Outlet	
	Mean	Stan Dev	Mean	Stan Dev	Mean	Stan Dev	Mean	Stan Dev
Total Al	178	17.5	180	17.9	46.7	2.1	45.7	2.1
Total Fe	284	134.9	271	110.6	148.5	37.2	94.1	52.7
Total Mn	1.51	.14	1.67	.23	1.2	0.1	1.3	0.3
Sulfate	2618	285	2683	201	1560	223	1551	218
pH	2.7	.27	2.58	.19	3.1	0.3	2.8	0.4
Specific Conductivity	3349	307	3440	194	2414	246	2559	278

NOTES: 1) All units mg/L except for pH (standard units) and Specific Conductance (u mho/cm).
2) All samples taken between July 10, 1986 and Sept. 30, 1987. Number of samples taken is 21.

TABLE 2
Typha latifolia Analysis Summary

	Total Al		Total Fe		Total Mn	
	Mean	Stan Dev	Mean	Stan Dev	Mean	Stan Dev
Rhizomes						
Control	558	506	590	333	42	31
Large Wetland	1398	1268	4237	1735	164	74
Small Wetland	1400	1478	4806	2325	134	72
Roots						
Control	5171	2368	8093	7584	475	813
Large Wetland	7444	5006	40884	25437	270	151
Small Wetland	4703	2659	34609	29491	241	292
Leaves						
Control	139	100	198	95	275	263
Large Wetland	232	91	287	62	1760	1455
Small Wetland	243	101	286	134	1053	766

NOTES: 1) All units ug/g.
2) All samples taken between Dec. 23, 1986 and Sept. 21, 1987. Number of samples taken is 9.

TABLE 3
Soil Analysis Summary

	Control Peat		Large Wetland Peat		Small Wetland Peat	
	Mean	Stan Dev	Mean	Stan Dev	Mean	Stan Dev
Total Al	9595	1665	12872	1726.1	15413	4606
Total Fe	6918	2358	29009	18364	60839	68291
Total Mn	113	50	160.6	242.7	98.4	74.7

NOTES:
1) All units in ug/g.
2) Number of samples for control peat is 2. Number of samples for Large and Small Wetland peat is 10.

TABLE 4
Construction Costs

Wetlands Construction Costs - 1986	Large Wetland (Dollars)	Small Wetland (Dollars)
Site Development/Inflow Control Facilities	$5,510	$4,125
Wetland Construction	5,655	2,335
Materials (in place)		
- Water	780	375
- Bentonite	975	750
- Limestone Gravel	4,260	1,470
- Peat	6,760	3,380
- Vegetation Sod Mats	440	220
Wetland Flow Control/Aeration Structures	3,430	2,940
Total	$27,810	$15,595
Wetland Surface Area (m^2)	418	111
Wetland Surface Area ($ft.^2$)	4,500	1,200
Wetland Cost/Area (dollars/m^2)	66.53	139.89
Wetland Cost/Area (dollars/ft^2)	6.18	13.00

would provide only a minor contribution to the total metal retention of a functioning system.

The peat has also concentrated metals in the system. Total aluminum, iron and manganese concentrations for both wetlands and the control peat are shown in Table 3.

Because the removal of the metals in both systems was unsuccessful, the limestone gravel in the channels downstream of each wetland became armored in less than two weeks. Although no specific tests were made, visual indications suggest that metals precipitation and pH buffering decreased after the armoring process was complete.

It was also observed that detention times in the systems were much shorter than was desired. Dye tests showed that the detention times were approximately seven hours and three hours for the Large and Small Wetlands, respectively. These low retention times are due primarily to the relative impermeableness of the peat once it is saturated.

WETLANDS CONSTRUCTION COSTS

Construction of the Large and Small Wetlands occurred during the months of July and August in 1986. Because of the relatively good access to the project sites many different pieces of equipment were used during construction, including bulldozers, backhoes, smooth-drum rollers, water trucks, motor graders, tractor-trailers, and rubber-tired front end loaders. Use of specialized equipment allowed for the volumes of material incorporated into the system to be easily handled and placed, and for work to be completed in less than four weeks.

Table 4 shows a breakdown of the costs for the construction of the Large and Small Wetlands. The breakdowns show that material costs made up the largest portion of the construction costs. The peat was the largest cost material item because it was necessary to haul it approximately 400 kms (250 miles) to the project site.

CONCLUSION

Two passive treatment systems constructed in Montana during 1986 have been ineffective in removing heavy metals from acid mine drainage. There seems to be two primary reasons for the ineffectiveness of these systems. Firstly, both systems were undersized, which resulted in very low retention times and limited the contact between the AMD and the primary heavy metal removal medium, the peat moss. Secondly, the systems designs did not force the AMD to flow through the peat at any location. The designs maximized the length of the flow paths through each system, but most of the flow through the systems was above the AMD-peat interface.

Improvements in the performance of these systems would probably be realized if the retention time was increased and provisions were made to force the AMD to flow through the peat. Expansions were made to both systems during the summer of 1987. These expansions significantly increased the size of each system and provided for flow of the AMD through the peat. A report on the performance of these expansions will be made at a future date.

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EFFECTS OF CATTAILS (TYPHA) ON METAL REMOVAL FROM MINE DRAINAGE[1]

J. C. Sencindiver and D. K. Bhumbla[2]

Abstract. -- Natural and constructed wetlands have been shown to ameliorate acid mine drainage, but mechanisms for metal removal in wetland treatment systems are not well understood. Therefore, seven natural cattail wetlands in Monongalia County and five in Preston County, WV, which received drainage from surface coal mines were selected for study. Aboveground plant biomass in each wetland was estimated and plant samples were collected in June and September 1986 to evaluate bioconcentration of Fe and Mn. Sediment samples were collected to determine pH, Eh, texture, and extractable Fe and Mn. Plant biomass of these wetlands was less than 50% of biomass reported in the literature for wetlands managed for biomass. The average aboveground (leaves and stems) uptake of Mn by cattails in the spring was 5.37 kg/ha and 5.20 kg/ha for Monongalia and Preston Counties, respectively. In the fall, Monongalia County cattails accumulated 11.47 kg/ha and cattails in Preston County accumulated 6.19 kg/ha. Concentrations of Mn in the rhizomes were much lower than concentrations of plant tops. Iron uptake by aboveground plant parts was very low, less than 4 kg/ha, for both counties at both sampling times. Concentrations of Fe in the rhizomes were 30 to 100-fold greater than Fe concentrations in the plant tops. Calculations show that cattails in these wetlands removed less than 1% of the total Fe added to the wetlands by mine drainage. The pe + pH values of the sediment where cattails were growing were less than the values for areas with no cattails, indicating that cattails may lower the redox potential of the wetland enough to precipitate Fe and Mn.

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INTRODUCTION

In the search for safe, cost-effective ways to treat acid mine drainage increasing attention has been focused on the use of cattail (Typha) wetlands (Girts and Kleinmann 1986, Snyder and Aharrah 1984), because these wetland systems are capable of removing Fe and Mn from the drainage. Due to saturated soil conditions and the presence of decomposable organic matter, the biochemical oxygen demand of most wetlands far exceeds the rate of oxygen diffusion into the sediments (Ponnamperuma 1972, Gambrell and Patrick 1978). Without oxygen, the sediments become highly reduced as microbial respiration proceeds, using electron acceptors such as Fe, Mn, and SO_4^{2-}.

Cattail plants have morphological features such as arenchyema tissues which aid in the transport of oxygen from aboveground parts to the roots, thereby enabling the plant to grow in highly reduced environments (Armstrong 1978, Hutchinson 1975, Sebacher et al. 1985). The direct ameliorative effect of cattails is due to metal removal by plant uptake from acid mine drainage. Metals taken up by the plants are subsequently retained in the detritus after senescence of the plants. The indirect effect of the cattails on water quality is related to the fact that they modify the chemical and biological environments of the sediments.

Little quantitative data are available to provide information about the relative importance of direct or indirect mechanisms on the water treatment capabilities of cattail wetlands. Before the relative merits of wetland treatment schemes can be fully evaluated, it is necessary to understand the movement, retention, and transformation of metals in wetland ecosystems. This information is vital for development of design criteria for building manmade wetlands for treatment of acid mine drainage. This investigation was undertaken a) to determine the biomass and elemental composition of cattails growing in naturally occurring wetlands receiving mine drainage, b) to determine the seasonal changes in plant biomass, plant elemental composition, and plant uptake of Fe and Mn, c) to determine the temporal changes in extractable metals in sediments of cattail wetlands receiving mine drainage, and d) to determine the effect of the cattail plants on redox environment of sediments within the wetlands.

MATERIALS AND METHODS

Natural cattail wetlands (major species Typha latifolia) which received drainage from reclaimed surface coal mines were selected for study in two counties in northern West Virginia. Seven wetlands were located in Monongalia County and five were located in Preston County. The wetlands ranged in size from 40 m^2 to 1500 m^2. Waynesburg coal seam had been mined at all of the Monongalia County sites, and Upper and/or Lower Freeport coal had been mined at the Preston County sites.

Plant populations in each wetland were determined by counting the number of plants per square meter. A 1 m x 1 m quadrat was randomly placed at five points in each wetland. All cattails within the quadrat were counted. The total aboveground portions (leaves and stems) and rhizomes of cattails were sampled near the water inflow, near the middle, and near the water outflow of each wetland. These samples were collected in June 1986 (Spring) and September 1986 (Fall). The plant samples were cleaned with distilled water and dried in a forced air oven at 65°C. Dried samples were ground in a Wiley mill having stainless steel blades. These samples were sent to Pennsylvania State University for Fe and Mn analyses, and analyzed on an Inductivity Coupled Plasmaspectrograph as described by Dahlquist and Knoll (1978). Some plant samples were also analyzed at West Virginia University for comparison. In this procedure (Ganje and Page, 1974), a 1.0-g sample of plant tissue was digested with 9.0 ml of 3:1 mixture of nitric and perchloric acids in a tall 200-mL beaker. The digested material was dissolved and brought to volume in a 50-mL volumetric flask with 0.1 N HCl. The concentration of metals in the solution were determined by atomic absorption spectrophotometry. Plant uptake of metals was calculated by multiplying tissue concentrations by biomass. Similar data were produced by both laboratories, so only one set of data is presented.

Sediment samples were collected from the same three points of cattail sampling. The sediment samples were collected with an auger to a depth of 10 cm from the soil-water interface and transferred to plastic bags. Soil pH and Eh for redox measurements were made in the fresh, wet sediments. Eh was measured by using a platinum electrode with Ag/AgCl reference electrode. Eh readings were noted when the drift in Eh was less than 5 mV/min. Sediment pH was measured with a standard glass electrode. The pe + pH values were calculated by dividing Eh by 59.2 and adding pH (Lindsay 1979). After pH and Eh were measured the sediments were air-dried and passed through a 2-mm sieve. Soil texture was determined by the pipette method (Soil Survey Staff 1972). Extractable Fe and Mn were determined by extracting the sediments with 0.1 N HCl using 1:10 ratio of sediment to extracting solution. The extracted elements were determined by atomic absorption spectrophotometry.

Additional samples for the study of effect of vegetation on pe + pH of the sediments were collected from one point outside and on the water entry side of each wetland. The pe + pH data were calculated as described above.

Monthly water quality samples were collected from November 1985 through January 1987 (unpublished data, Dr. Henry Rauch, Department of Geology and Geography, West Virginia University). In general, the Monongalia mine water was near neutral pH. The lowest pH at any sampling time was 6.3 and the highest was 8.2. In Preston County, the mine water tended to be somewhat more acid. Only one site consistently had pH values above 6.0. Water pH at all other sites was generally below 6.0 and commonly between pH 3.0 and 4.0. Total Fe and Mn varied, but the Preston County mine water generally contained slightly more of these metals than the Monongalia County mine water.

Statistical analysis (ANOVA) was done using SAS programs, and significance between counties and seasons was tested at alpha levels of 0.05.

RESULTS AND DISCUSSION

Primary Biomass Production of Cattails.

The direct or indirect ameliorative effect of cattail wetlands on acid mine drainage passing through them is related to primary biomass production within the wetland ecosystem. Biomass data for wetlands in this study are presented in table 1. Dry matter yield was used as an index for biomass production, and it was computed from plant density and dry matter yield per plant (plant vigor). Plant density in Monongalia County wetlands was significantly greater than in Preston County wetlands. Cattail growth in wetlands of Monongalia County was significantly more vigorous than the cattail growth in Preston County wetlands at both sampling times. During the spring season the mean per plant dry matter production in Monongalia County wetlands was 2.5 times the dry matter yield per plant in Preston County. At the fall sampling, the plant vigor in Monongalia County was 2.2 times greater than that of Preston County.

Biomass production was three times higher in Monongalia County than in Preston County at the spring sampling and almost three times higher at the fall sampling. Biomass production depended on plant density and plant vigor. Low levels of biomass production were caused by low plant density. Both plant vigor and biomass were significantly higher in fall-harvested cattails than in spring-harvested cattails.

When the dry matter production of cattails in this study was compared to the dry matter production in fertilized cattail stands managed for biomass production in Minnesota, Wisconsin, and Texas, the amount of dry matter produced by natural wetlands in this study was less than 50% of that produced in the managed wetlands (Bonnewell and Pratt 1978, Pratt and Andrews 1980). Thus, there is a great potential for increasing biomass production in cattail wetlands by proper management. The productivity of cattail wetlands is related to the nutritional status and biochemical environment of the substrate in which the cattails are growing. In general lower biomass production in Preston County was related to the pH of the sediment (table 2). A significant positive correlation coefficient (r = 0.73)

Table 1 -- Plant density, plant vigor, and biomass production of cattails in wetlands receiving mine drainage.

Property	Season	Monongalia Co.	Preston Co.
Plant density (plants/m^2)	Spring	12.9[1] 7.9 - 15.9[2]	7.9[1] 0.7 - 19.2[2]
Plant vigor (g dry matter/ plant)	Spring	39.0 20.1 - 81.7	16.5 11.0 - 24.2
	Fall	45.5 25.3 - 91.5	20.6 13.2 - 31.4
Biomass (g dry matter/m^2)	Spring	411.9 211.9 - 663.0	146.2 5.8 - 345.0
	Fall	554.3 264.5 - 1180.2	191.8 7.8 - 446.7

[1] Mean of seven sites in Monongalia County and five sites in Preston County.

[2] Range.

was observed between sediment pH and biomass. Other factors such as low sediment concentration of P could also have affected biomass production.

Table 2 -- Properties of sediment in cattail wetlands receiving mine drainage.

Property	Season	Monongalia Co.	Preston Co.
pH	Spring	7.93[2] 7.64 - 8.11[3]	4.67[2] 2.34 - 6.07[3]
Iron[1]	Spring	5343 1992 - 10154	3503 1306 - 7616
	Fall	6418 2436 - 13,550	5625 2464 - 10,850
Manganese[1]	Spring	1536 430 - 2216	280 50 - 713
	Fall	1412 422 - 2617	357 53 - 697

[1] 0.1 N HCl extractable iron and manganese (ug/g).
[2] Mean of seven sites in Monongalia County and five sites in Preston County.
[3] Range.

Properties of Sediments.

Wetland sediments have a natural tendency to converge to pH 7.0, irrespective of the initial soil pH (Sajwan and Lindsay 1986). In Preston County wetlands, sediments with pH values lower than 7.0 indicated the presence of nonequilibrium conditions, i.e. these sediments represented the wetlands which were constantly receiving an influx of highly acidic water.

There were significant differences in the extractable Mn concentrations between the sediments of Monongalia and Preston Counties (table 2). Extractable Mn concentrations in the Preston County sediments were significantly lower than Mn concentrations in sediments of Monongalia County. The correlation coefficient between the aboveground plant tissue Mn concentrations and concentration of extractable metals in the sediment was 0.52 which was nonsignificant.

No significant differences in the amounts of extractable Fe in sediments were found between counties or between seasons (table 2). No significant correlation was found between the amount of metals extracted from the sediment and the concentrations of the metals in the plant tissue. This lack of correlation was probably due to the nature of the substrate for plant growth. In wetlands receiving acid mine drainage, the extractable metals are indicators of the capacity factor for plant nutrition, i.e. the amount of metal which can be potentially taken up by the growing plants. The actual amount of metal removal by the plant is dependent on the intensity factor, i.e. the concentration of metal in the soil solution. In normal plant growth media the intensity factor is governed by the capacity factor, but in wetlands receiving acid mine drainage the intensity factor is largely independent of the capacity factor due to differences in water chemistry of the drainage and sediment and to continuous influx of metals into the growth media. This continuous flow of mine drainage into the system is responsible for the lack of a significant correlation between extractable metals and concentrations in plant tissue.

Texture of the sediments in the Monongalia County wetlands was sandy loam, silt loam, or clay. Texture of wetland sediments in Preston Coundy was either clay loam or silty clay loam. These textures probably represent the textures of the surrounding minesoils.

Concentration and Uptake of Manganese and Iron in Cattails.

Manganese

The plant tissue analyses for Mn (table 3) suggest another reason for the yield differential between cattails growing in Preston and Monongalia Counties. The lower cattail yields in Preston County could be due to the high levels of Mn in the plant tissue. There was a significant increase in the plant tissue concentrations of Mn from spring to fall samples for Monongalia County, but the seasonal concentration differences were not significant for Preston County. This lack of increase in Mn concentration with growing season in Preston County is possibly due to the fact that the concentrations during the spring season had already reached the maximum value for bioconcentration in the cattail, so there could not have been any further concentration increases.

Table 3 -- Concentration and uptake of manganese in cattails sampled from wetlands receiving mine drainage.

Plant Parts	Season	Monongalia Co.	Preston Co.
Rhizomes (ug/g)	Spring	665[1] 625 - 705[2]	885[1] 498 - 1278[2]
	Fall	795 567 - 972	684 394 - 1119
Leaves + Stems (ug/g)	Spring	1202 702 - 1824	3109 1879 -4071
	Fall	2202 586 - 2912	3189 2653 - 3970
Leaves + Stems (kg/ha)	Spring	5.37 2.64 - 7.92	5.20 0.11 - 11.60
	Fall	11.47 3.72 - 23.22	6.19 0.25 - 15.95

[1] Mean of seven sites in Monongalia County and five sites in Preston County.
[2] Range.

During the spring season the mean Mn concentration in cattails of Preston County was 2.5 times greater than the mean Mn concentration in cattails of Monongalia County (table 3). Even with these large differences in concentrations of Mn the differences in uptake of Mn at the spring sampling between counties were statistically nonsignificant. This lack of a sizable difference in uptake is related to low biomass production in cattail wetlands of Preston County.

Rhizome samples were too few for statistical analyses. In general the concentrations of Mn in the rhizomes were lower than the concentrations in the leaves and stems (table 3). In Preston County the concentration differences between rhizomes and aboveground plant portions were four-fold or greater.

Iron

Fe concentrations in cattail tissues in Preston County were significantly different at both sampling times from those in Monongalia County (table 4). Iron concentration in Preston County cattails was 3.4 times greater than Fe concentration in Monongalia County cattails in the spring, but this difference was reversed at the fall sampling. At the fall sampling Fe concentration in Monongalia County cattails was 9.2 times greater than Fe concentration in Preston County cattails. These seasonal differences could be due to the formation of iron oxide coatings that were observed on the roots of cattails growing in Preston County.

Under reducing conditions, Fe^{2+} is thought to be oxidized to the less soluble Fe^{3+} by oxidative agents released from the roots, thus creating a coating or plaque of an insoluble Fe^{3+} compound on the root surface (Taylor et al. 1984). Iron oxide coatings are a survival mechanism for cattails growing in a contaminated environment, because the coatings do not allow further uptake of Fe (Taylor and Crowder, 1984, Taylor et al. 1984). Since no additional Fe was taken up by the plant, Fe concentration decreased as the plant continued to grow. Plants growing in Monongalia County may have continued taking up Fe during the growing season. The high concentrations of Fe found in Preston County rhizomes (table 4) are probably due to the coatings.

Seasonal differences in Fe uptake were significant for the cattails growing in Monongalia County while they were not significant for cattails in Preston County. In absolute terms, the amounts of Fe removed by plants were extremely low, i.e. 2.67 and 3.74 kg/ha for the spring and fall sampling periods in Monongalia County. The amounts taken up in Preston County were smaller, i.e. 1.07 kg/ha and 0.76 kg/ha for the spring and fall sampling, respectively.

Table 4 -- Concentration and uptake of iron in cattails sampled from wetlands receiving mine drainage.

Plant Parts	Season	Monongalia Co.	Preston Co.
Rhizomes (ug/g)	Spring	--- ---	15,288[2] 9648 - 19,506[3]
	Fall	5392[2] 1000 - 10,818[3]	11,170 8036 - 14,650
Leaves + Stems (ug/g)	Spring	595 109 - 1539	2043 213 - 5369
	Fall	1919 409 - 7352	208 88 - 344
Leaves + Stems (kg/ha)[1]	Spring	2.67 0.23 - 5.47	1.07 0.04 - 2.80
	Fall	3.74 1.56 - 5.31	0.76 0.06 - 1.31

[1] Uptake in kg/ha was calculated by multiplying concentration (ug/g) by biomass.
[2] Rhizome data are means of four sites in each county. All other data are means of seven sites in Monongalia County and five sites in Preston Co.
[3] Range.

Removal of Iron from Water by Cattail Plants.

In order to calculate total removal of Fe by cattails, biomass of the aboveground and belowground parts of the plants must be known. Biomass of rhizomes was not determined in this study, so it was estimated. Biomass of Typha latifolia rhizomes varies but it is commonly 50% of the total biomass (Personal communication, Dr. D.C. Pratt, Botany Department, University of Minnesota). Therefore, for our calculations, we assumed that aboveground and belowground biomass were equal.

To calculate an example of Fe removal by cattails in this study, a site in Preston County was chosen because it had the highest concentration of Fe (19,506 ug/g) in the rhizomes. Aboveground and belowground biomass each equal 287.2 g/m^2.

To estimate uptake by the rhizomes, biomass must be multiplied by the Fe concentration. So, 287.2 g/m^2 X 19,506 ug/g = 5,602,123.2 ug/m^2, or approximately 56 kg/ha of Fe were removed by the rhizomes during the growing season.

This site had a median flow rate of 0.5 L/sec, so 15,768,000 L/yr will flow into this Preston County wetland. The median concentration of Fe entering this wetland was 10 mg/L. Therefore 157,680,000 mg/yr or 157.7 kg of Fe per year will be added to this wetland. Since the area of this wetland is 61.27 m^2, additional calculations show that approximately 25,700 kg/ha of Fe will enter this wetland during a year. Since the cattail plants are removing only 57.31 kg/ha (56 kg/ha for the rhizomes and 1.31 kg/ha for the tops), the plants are removing only about 0.2% of the total Fe entering the wetland.

Effect of Cattail Wetlands on Redox Environment.

Metals can be removed from water by various mechanisms, and data on the redox environment within a cattail wetland may give some information on possible mechanisms of removal. Sediment of one site in Preston County, had a positive Eh of 230 mV, but the Eh of sediments at all other sites ranged from - 247 to - 18 mV. These Eh values suggest that reduction may be a major mechanism for the removal of iron. The pe + pH values of the sediments with cattails were close to 4.24 (table 5), where SO_4^{2-} and Fe^{3+} can be reduced to form insoluble FeS_2 at pH 7.0 (Lindsay 1979).

The role of cattails in enhancing the reduced environment in wetlands was confirmed when redox potentials were determined in wetland sediments with and without cattails (table 5). The data indicate that the presence of cattails has a significant effect on redox environment, making it more reducing. Cattails can lower the redox potential of the sediments enough to precipitate Fe in its sulfide form.

Table 5 -- Redox environment in sediment of cattail wetlands receiving mine drainage.

Property	Monongalia Co.	Preston Co.
pH	7.95[1] 7.64 - 8.11[2]	4.63[1] 2.34 - 6.07[2]
pe + pH (with cattails)	4.57 3.93 - 5.36	4.31 2.62 - 6.20
pe + pH (without cattails)	10.63 8.79 - 13.25	9.82 4.97 - 13.27

[1] Mean of seven sites in Monongalia County and five sites in Preston County.
[2] Range.

CONCLUSIONS

Amounts of metals removed from mine drainage by cattail wetlands depend upon cattail biomass and concentration of metals in plants. In this study biomass production appeared to be related to the quality of the sediment in the wetland. Low pH and high Mn levels were related to reduced cattail biomass in some wetlands. To increase metal removal from mine drainage by plant accumulation, emphasis should be placed on increasing dry matter production rather than on increased bioconcentration.

Data from this study also indicate that plant uptake is not a major mechanism for the attenuation of metals in mine drainage. Eh values and pe + pH calculations show that cattail wetlands have reducing environments. The presence of cattails in a wetland actually promotes a more reducing environment. Chemical reduction within the wetland may be a mechanism by which metals like Fe are removed. Additional research will be required to determine other possible mechanisms of metal removal from mine drainage flowing through cattail wetlands.

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WATER AND SOIL PARAMETERS AFFECTING GROWTH OF CATTAILS; PILOT STUDIES IN WEST VIRGINIA MINES[1]

David E. Samuel, John C. Sencindiver, and Henry W. Rauch[2]

Abstract.--Although it has been shown that cattail-dominated wetlands reduce manganese and iron content of acid mine drainage, little is known about the effects water and soil parameters have on the growth of cattails (Typha latifolia). Knowledge of such parameters for vegetation growth is essential for planned construction of wetlands. Three pilot studies were done to: (a) survey water quality where cattails grow naturally, (b) compare water and soil parameters from sites where cattails were found to immediately adjacent spots where no cattails were found, and (c) determine the effects of wetland vegetation on total iron and manganese concentrations and removal in water as compared to an identical site with no vegetation. In June 1986 water quality parameters were measured at 26 sites with cattails and 30 nearby sites without cattails in northern West Virginia Water pH was below 2.5 at six cattail sites and below 2.0 at one site. Only three cattail sites had water with over 100 ppm total iron. Comparison of 10 of the above-mentioned locations, without any vegetative growth, and seven adjacent spots with cattails showed that only total iron in water was significantly lower in cattail versus non-cattail sites. Data also suggest that lower pH and higher aluminum content present problems for cattail survival and germination. To determine the effects of wetland vegetation on iron and manganese removal two watertight boxes (16 ft by 4 ft by 1 ft) were constructed side-by-side in a cattail marsh. Sediment was placed in both boxes and 228 cattails were transplanted to one on June 17, 1986. Water entering each box at a flow of 1 gal/min had total iron concentrations of approximately 20-25 ppm and Mn concentrations of 15-20 ppm. Adult cattails died, but new sucker growth yielded 261 cattails by August 1986. There were 194, 293, and 295 cattails in April, May, and June 1987, respectively. From October 1986 through May 1987, there was an average decrease of 3.14 ppm in total iron in cattails and 0.04 ppm in the control box. During the same period there was no significant decrease in manganese in the cattail box (average decrease of 1.9 ppm), or the control. There were no changes in pH in either box during the study. From the results of these three studies, it appears that cattails, and perhaps any wetland vegetation, play some role in providing an ecological system which functions to remove iron.

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INTRODUCTION

Cattail-dominated wetlands have been shown to reduce manganese (Kleinmann et al. 1985), and iron (Kleinmann 1985, Brodie et al. 1985). Another reason for utilizing cattails in manmade wetlands is because survival is high. Fulton et al. (1983) found that cattail survival after transplanting by various procedures was higher (survival was 78%) than 11 other wetland species.

These pilot studies were precipitated by discussions with consultants building wetlands for industry to improve water quality. Little, if anything, is known about the various water quality or soil chemical properties that may limit the growth of wetland plants, including cattails. This information is needed so that these limitations to growth can be overcome when building wetlands to treat acid mine drainage. While conducting other field studies, we noted other sites where cattails were growing immediately adjacent to, and in the same substrate and seep as, areas where no cattails were growing. Therefore, the following three pilot studies were done to: (a) survey water quality where cattails grow naturally; (b)compare water and soil parameters from sites where cattails were found to immediately adjacent spots where no cattails were found; and (c) determine the effects of wetland vegetation on total iron and manganese concentrations and removal in water as compared to an identical site with no vegetation.

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MATERIALS AND METHODS

Between June 19 and June 26, 1986, water samples were taken at 56 sites near Morgantown. Sites were selected which had cattails growing. If an adjacent site appeared to have the same flow of water and the same substrate, but no cattails growing, then it was sampled. In addition, other isolated sites with no cattails that appeared to have good water flow and a mud substrate were sampled. Water temperature was measured at each site to the nearest 0.5°C. Readings were made within 1 second of removing the thermometer from the water. Water temperature was used in standardizing pH and conductivity meters.

Electrical conductivity was measured with an 18-volt Fisher conductivity meter, Model No. 152. A Fisher mini pH meter, Model No. 640, was used to measure water pH. Prior to each pH measurement the meter was standardized to Ph 4 and pH 7 buffers which had been allowed to equilibrate at water temperature. The combination electrode was cleaned with distilled water between each buffer and each water measurement. Water flow velocity and depth were measured for flow rate calculations to be made at a later time.

Two water samples were collected in 250-mL nalgene bottles at each sampling point. One of these samples was filtered through pre-weighted metrical membrane filters, pore size 0.45 um. Both samples were treated with 1 mL of 50% nitric acid to fix metals. A third unfiltered, unacidified water sample was collected in 1-L plastic cubitainers.

In the laboratory, unfiltered, acidified water samples were used to determine concentrations of total iron and manganese cations, and of Ca^{+2}, Mg^{+2}, Na^{+1}, and K^{+1}. Filtered, acidified samples were used to determine dissolved iron and manganese levels. Cation concentrations were determined by atomic absorption spectro-photometry by ASTM Method D2576 (ASTM 1976a).

In the course of collecting information for the first objective of this study, four sites of interest were noted. These sites had dense stand of cattails growing naturally, but there were small spots, either adjacent to or within the wetlands, that had no cattails. On September 3, 1986, soil and water samples were taken at 17 locations within these four sites. Methods of water analysis were identical to those outlined above. Sediment samples were taken from the same points as water samples, usually in the middle of the cattails wetland or in the nonvegetated areas. Sediment samples were collected with an auger to a depth of 10 cm from the soil-water interface and transferred to plastic bags. In the laboratory, cations were extracted by the double-acid method of Baker and Amacher (1982) and determined by atomic absorption spectrophotometry. Phosphorous was extracted by the method of Boltz and Howell (1978) and measured on a UV-VIS spectrophotometer.

To study the effects of wetland vegetation on iron and manganese removal, two plywood boxes were constructed in the middle of a cattail marsh in Greene County, PA on June 17, 1986. The marsh is approximately 4 acres in size and had an average water pH of 2.85, total iron of 25 ppm, and total manganese of 16 ppm (based on samples taken, three locations in three seasons).

The boxes were 16 ft by 4 ft by 1 ft in size, and were imbedded 1 ft deep in the marsh, adjacent to each other. They were placed so that there was a slight flow of water from one end to the other. Inflow pipes allowed flow of about 1 gal/min. Sediment from the marsh was placed into the

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boxes as substrate. In one box adult cattail plants were carefully transplanted at the same density found in the marsh (3.5/ft^2) making a total of 228 cattails. The other box remained devoid of all vegetation. Water samples were taken at the inflow and outlfow of each box on June 20 and approximately every month thereafter for a year (sampling in December 1986 and February 1987 was not possible due to weather conditions). Counts of cattail density were made periodically as well. Sediment samples were taken in July 1987.

RESULTS AND DISCUSSION

Where cattails grow.--Water at cattail sites had a wider range of pH than water at non-cattail sites (fig. 1). Cattail sites had a mean pH of 4.85, while non-cattail sites had a mean pH of 3.26. A wetland consultant (B. Pesavento, personal communication) indicated that only rarely were cattails found in water with pH below 2.5 or an iron concentration above 100 ppm. Forty-two percent (11/26) of the cattail sites in this study had a water pH below the 3.26 mean, with six sites below pH 2.5 and one below 2.0. This suggests that cattails will tolerate lower pH, and pH alone may not be a limiting factor for the establishment of this plant.

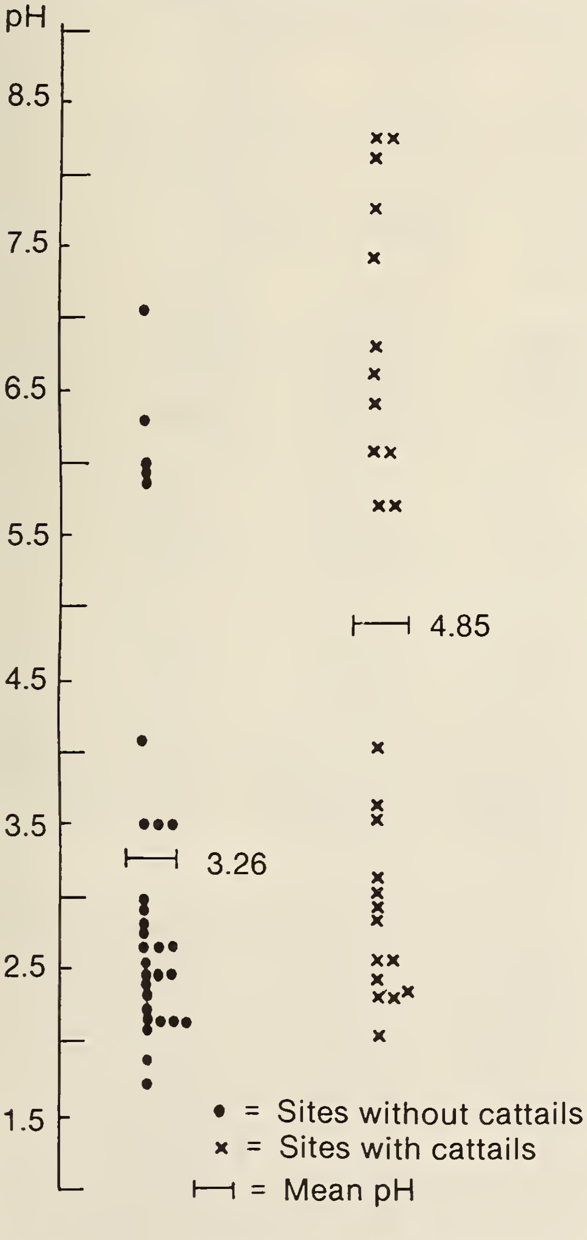

Figure 1.--pH levels of water samples taken at 56 sites in northern West Virginia.

There appears to be a relationship between iron concentrations and the presence or absence of cattails (fig. 2). More often sites with lower concentrations of total iron in water had cattails; 57% (15/26) of the cattail sites had iron levels below 25 ppm, as compred with 13% (4/30) of the non-cattail sites. In contrast 36.7% (11/30) of the non-cattail sites had iron concentrations over 101 ppm (table 1).

There were only three cattail sites with iron concentrations of over 100 ppm, with the highest being 144 ppm (table 1). On that site only scattered cattails were found. A second site with 113 ppm iron had only four scattered cattail plants while another site with 113 ppm iron had a dense stand of cattails.

There may well be a combination of factors that affect cattail growth. When the sites without cattails were ranked by increasing water pH (table 2), there was higher total iron at the lower pH levels. There were nine sites with pH less than 2.3 (fig. 1). The average total iron for the eight non-cattail sites with pH below 2.30 was 233.7 ppm while average total iron for eight non-cattail sites with pH above 3.51 was 73.5 ppm (table 2). Iron levels of sites with pH between 2.30 and 3.51 were highly variable (table 2). When the low pH sites with no cattails were compared to the low pH sites with cattails, it was noted that iron levels were lower in the cattail sites (table 2). Seventeen of 26 sites with cattails had pH above 3.00, and only three of those had iron levels of 73 ppm or above (table 2). Average total iron for the 12 cattail sites with pH above 4.02 was only 27.9 ppm (table 2).

No other measured water quality parameters (Mn, K, Na, Ca, Mg) showed any notable trends between sites with and without cattails.

PAIRED SITES

Water and soil samples were taken on a paired basis when possible (i.e., one sample from a cattail site and another sample from an adjacent spot without cattails) to test for additional differences associated with cattails. Only total iron in water samples was significantly different (Wilcoxon's sign rank $p < 0.055$) between sites with

Table 1.--Sites with and without cattails ranked by Fe concentration in water. All values are in ppm units except for pH.

Without Cattails			With Cattails		
Fe	pH	Mn	Fe	pH	Mn
747.00	2.07	34.00	144.00	5.70	7.30
537.00	1.84	11.30	113.00	2.85	3.56
211.30	2.91	9.30	113.00	2.85	3.56
169.00	2.36	2.85	91.77	2.05	10.08
152.00	3.51	3.78	91.00	2.30	15.10
153.70	2.15	9.12	90.00	5.70	6.90
133.00	2.14	3.03	73.00	6.78	10.30
123.00	5.90	5.50	70.00	2.30	3.55
122.00	2.98	1.11	59.10	2.36	6.60
116.60	3.57	13.09	32.00	4.02	14.50
103.00	2.45	2.28	28.16	2.42	16.94
93.00	1.70	7.40	14.90	3.67	4.10
89.67	2.13	14.63	12.06	2.54	18.92
88.62	2.20	9.90	10.60	3.12	51.80
86.00	5.87	5.56	9.80	6.10	2.30
85.00	4.11	15.10	8.10	6.41	1.46
78.00	3.54	4.22	7.06	2.55	
63.50	2.79	7.70	4.98	3.56	15.80
63.00	6.32	1.76	4.43	8.25	0.42
60.00	2.33	6.30	3.45	3.03	5.40
47.63	2.66	6.36	2.14	8.10	0.24
39.00	5.99	7.80	1.44	6.10	0.34
38.60	2.54	11.10	1.05	7.40	0.12
30.80	2.43	4.19	0.39	6.63	2.41
27.94	2.19	17.05	0.14	8.25	0.01
25.20	2.47	7.40			
24.40	2.66	15.20			
23.00	2.81	21.90	0.02	7.78	0.04
23.00	2.65	24.90			
0.38	7.06	2.41			

cattails (53.8 ppm mean iron) and adjacent sites without cattails (98.2 ppm mean iron) (table 3). For soil samples, significant differences occurred for Ca (p 0.062) and Mn (p 0.062), with higher levels of both elements present in sites with cattails (table 3). These differences were affected by the small sample sizes and great variation in samples. For example, the high soil Mn level found in cattail sites was due to one site's having 184 ppm and a second having 57.6 ppm of Mn. No other cattail site soil samples contained more than 12.2 ppm Mn. One cattail site had 228 ppm K, but no other sites were higher than 21.2 ppm. Ca levels in soil samples from cattail sites seemed inflated as well, due to two samples of 1074 and 752.

B. Pesavento (personal communication) suggested that aluminum may be toxic to cattails with low water pH. Aluminum was not measured in water samples, but it was in soil samples. The ratio of the average pH/Al for 10 soil samples from non-cattail sites was .143, while the same ratio from 7 cattail sites was .240. Thus, it appears that lower pH and higher Al of the soil may present problems for cattail germination or survival.

It is obvious from table 3 that no one soil or water parameter exhibits low or high levels when cattails are present compared to when they are absent in the adjacent sites. At several adjacent sites (one with and one without cattails), it was noted that both had high pH and low iron concentrations in both soil and water samples. Other parameters such as soil Al were similar. One pair of samples showed low water pH (2.8-3.0), and high iron (120-150 ppm) in the water, and similarly had low soil pH and high soil iron levels. Yet cattails thrived in one place and were totally absent -- as was all vegetation -- immediately adjacent. In fact, there was a distinct demarcation between the area with

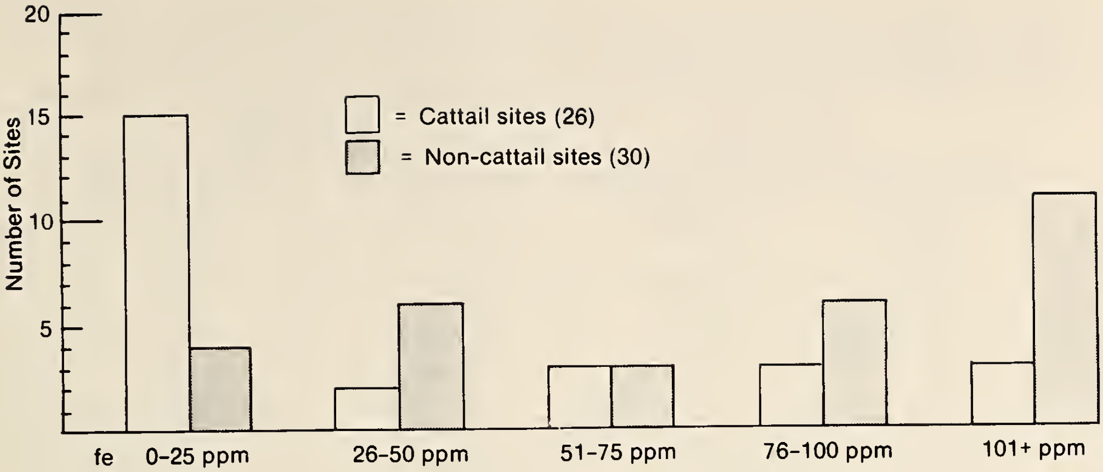

Figure 2.--Iron concentrations in water samples taken at 56 sites in northern West Virginia.

Table 2.--Sites with and without cattails ranked by pH value. All values are in ppm units except for pH.

Without Cattails			With Cattails		
pH	Fe	Mn	pH	Fe	Mn
1.70	93.00	7.40	2.05	91.77	10.08
1.84	537.00	11.30	2.30	91.00	15.10
2.07	747.00	34.00	2.30	70.00	3.55
2.13	89.67	14.63	2.36	59.10	6.60
2.14	133.00	3.03	2.42	28.16	16.94
2.15	153.70	9.12	2.54	12.06	18.92
2.19	27.94	17.05	2.55	7.06	
2.20	88.62	9.90	2.85	113.00	3.56
2.33	60.00	6.30	2.93	113.00	4.92
2.36	169.00	2.86	3.03	3.45	5.40
2.43	30.80	4.19	3.12	110.60	51.80
2.45	103.00	2.28	3.56	4.98	15.80
2.47	25.20	7.40	3.67	14.90	4.10
2.54	38.60	11.10	4.02	32.00	14.50
2.65	23.00	24.90	5.70	144.00	7.30
2.66	47.63	6.36	5.70	90.00	6.90
2.66	24.40	15.20	6.10	9.80	2.30
2.79	63.50	7.70	6.10	1.44	0.34
2.81	23.00	21.90	6.41	8.10	1.46
2.91	211.30	9.30	6.63	0.39	2.41
2.98	122.00	1.11	6.78	73.00	10.30
3.51	152.00	3.78	7.40	1.05	0.12
3.54	78.00	4.22	7.78	0.02	0.04
3.57	116.60	13.09	8.10	2.14	0.24
4.11	85.00	15.10	8.25	4.43	0.42
5.87	68.00	5.56	8.25	0.14	0.01
5.90	123.00	5.50			
5.99	39.00	7.80			
6.32	63.00	1.76			
7.06	0.38	2.41			

Table 3. Mean water and soil quality parameters (ppm) for ten sites without cattails and seven adjacent sites with cattails.

	Water Analysis		Soil Analysis	
	Cattail Sites	Non-cattail Sites	Cattail Sites	Non-cattail sites
pH	3.94	3.87	4.54	3.87
Fe	53.8	98.2	133.6	93.0
Mn	6.3	6.2	43.6	4.4
K	8.7	7.7	49.0	8.9
Na	18.4	15.8	NS	NS
Ca	201.5	190.1	439.1	123.0
Mg	76.2	68.1	17.5	10.0
Al	NS	NS	17.9	25.7
Po	NS	NS	5.9	3.8
Zn	NS	NS	19.8	1.6
Cu	NS	NS	0.5	0.4

NS -- Not sampled.

cattails and that with none, within the same seep. This was found at several locations even though no individual paired water or soil parameters were significantly different.

CATTAIL AND CONTROL BOXES

There has been speculation both in academic settings and in the literature, about the role of wetland plants in the complex process of removing iron and manganese from acid mine drainage. Cattail plants remove some iron from the environment (Snyder and Aharrah 1984), and it is known that complex bacterial reactions also lead to removal of certain metals from water. Some (e.g., B. Pesavento, personal communication) believe that the species of wetland plants is of little consequence in improving water quality and that the entire wetland ecosystem provides the ecological basis for removal of iron and manganese. Thus, the plants and the soil provide the environment for algae and bacteria to remove metals through complex oxidation and reduction reactions.

There were 228 cattails initially planted in the 64-ft^2 box on June 17, 1986. Three months later, many of the adult plants had died, but new sucker growth resulted in 261 cattail plants present. Counts were also made the first week of April, May, and June 1987, yielding 194, 293, and 295 cattails, respectively. There was an increase in plant density from 3.56 cattails ft^2 to 4.61 cattails ft^2 in one year.

Monthly water samples were compared for two periods. The first sample was taken two days after construction of the boxes and placement of substrate and cattails. Other samples in this first period were taken in July, August, and September 1986. In late September, an abandoned surface mine located above the wetland was opened and water was treated. This caused an increase in pH, and a decrease in iron and manganese entering the inflow of the cattail and control box. Thus, a second period was established for data analysis beginning in early October 1986, and running until May 1987. There was no significant change in iron or manganese during the first period (June-September 1986) for either the cattail box or the control box (table 4).

For the second period (October 1986-May 1987), there was no significant average decrease in the difference ($p > 0.05$) between the inflow and outflow for iron in the cattail box (decrease of 3.14 ppm iron) or the control box (decrease of 0.04 ppm iron).

Excluding the first sample, which was taken two days after the wetland was constructed, the cattail site showed a reduction in iron from inflow to outflow in eight of nine samples taken (average monthly decrease of 3.46 ppm). Excluding the first

Table 4. Average inflow and outflow levels (ppm) of iron and manganese in a 16-ft by 4-ft system with a flow of 1 gal/min. One system had cattails and one had no cattails. In analysis, there were two periods*: first, June 20-Sept. 16, 1986 (four samples**); second, Oct. 6, 1986-May 21, 1987 (six samples).

	IRON		MANGANESE	
First Period:	Inflow	Outflow	Inflow	Outflow
Cattails	19.53	17.70	19.15	20.23
No Cattails	20.67	18.90	18.57	20.37
Second Period:				
Cattails	7.77	4.63	12.98	11.08
No Cattails	5.42	5.38	12.08	12.32

* In late September a mine became active above this wetland, and water was treated, which raised the pH and lowered the iron and manganese. Thus, data are separated.

**First sample in this period was taken two days after the wetland was constructed.

sample, the control site showed a reduction in iron from inflow to outflow in four of nine samples (average decrease of 1.43 ppm).

During the first period, manganese increased an average of 1.08 ppm for the cattail wetland and 1.80 ppm for the control from inflow to outflow. During the second period (six samples taken) manganese increased at the outflow (average of 0.24 ppm) in the control but decreased (insignificant average of 1.90 ppm at .05 level) at the outflow of the cattail wetland. The pH range at the inflow was 2.85 to 3.26 for the first period and 3.65 to 6.87 for the second, with no significant difference in the average monthly change for the cattail box or the control at the outfall.

Though preliminary, it appears that cattails aid removal of iron. After the cattails had been planted and were growing for 3 months, there was an average monthly decrease in iron from inflow to outflow of 3.14 ppm. Since only 0.04 ppm was removed during this same time in the control, which contained sediment only, the plants must play some role in providing an ecological system which functions to remove iron.

Soil samples were taken at the inflow and the outflow of the cattail and control boxes in August 1987 (table 5). Highest levels of soil iron were found at the outflow of the cattail box. Levels of soil iron were considerably higher in soils found in the box with cattails than the box with sediment and no cattails.

CONCLUSIONS

While its true that iron levels on cattail sites might be lower due to the plants removing iron, chances are that the plants germinate and grow better in areas of lower iron and higher pH.

The paired sites were interesting because of the abrupt demarcation within the wetland. Bare spots with no vegetation were found in the middle of heavy growth of cattails. In some of these paired sites the soil and water iron and pH levels were almost identical yet cattails grew in one site and not the other. How the various levels of metals in the soil and water affect plant germination will require an intensive laboratory study. Even then interactions between various parameters might occur that make results difficult to interpret.

The boxes with cattails and no vegetation showed differences in ability to remove iron. A study on the relationship to cattails, and other vegetation, to bacterial production would be most beneficial. These pilot studies will not provide answers, but they do give us some further direction for study.

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Table 5. Soil concentrations (ppm) at the inflow and outflow of the cattail box and the control box, sampled August 4, 1987. Two samples were taken in the wetland near the boxes, and averaged.

	Fe	Mg	Al	pH
Cattail Box				
Inflow	71.70	6.52	82.50	3.62
Outflow	201.50	7.92	68.10	3.20
No Cattail Box				
Inflow	52.20	5.26	75.30	3.97
Outflow	81.40	4.81	21.90	3.68
Surrounding Wetland	155.00	15.40	53.80	3.87

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DETERMINING THE CAPACITY FOR METAL RETENTION IN MAN-MADE WETLANDS CONSTRUCTED FOR TREATMENT OF COAL MINE DRAINAGE[1]

R. Kelman Wieder[2]

Abstract.--Within the past several years, there has been a tremendous increase in the use of man-made wetland systems for the treatment of acid coal mine drainage. However, quantitative estimates of the long-term capacity of a wetland for metal retention are lacking. In this paper, an upper limit for Fe retention in Sphagnum wetlands is estimated by individually considering the biological and chemical processes contributing to metal retention in wetland ecosystems. Also, different field monitoring schemes are discussed in terms of their potential for assessing the effectiveness of metal retention in man-made wetland systems and their potential for extrapolating the long-term capacity for effective treatment of mine drainage. Although it has been suggested that man-made wetlands may offer a low-cost approach to mine drainage treatment, cost/benefit analyses cannot be carried out without being able to reliably estimate long-term capacity for metal retention in a man-made wetland system given a particular volume and chemistry of mine drainage water. Until long-term capacity for metal retention in man-made wetlands can be reliably predicted, the environmental and economic potential of wetland treatment of coal mine drainage remains difficult to assess.

INTRODUCTION

One of the most frequently cited values of freshwater wetlands is their ability to act as nutrient sinks, improving the quality of water that flows through them (Greeson et al. 1978). This characteristic has been exploited in using freshwater wetlands for nitrogen and/or phosphorus removal from wastewaters (Kadlec and Tilton 1979, Godfrey et al. 1985). Whereas denitrification is mainly responsible for nitrogen removal from wastewaters in wetlands, phosphorus retention is accomplished mainly by adsorption and precipitation reactions with Al, Fe, and Ca in the soil (Nichols 1983). As such, nitrogen removal does not necessarily decline with time, but the capacity of wetland soils to retain phosphorus is limited, and phosphorus retention in wetlands decreases over time (Richardson 1985).

Freshwater wetlands may also act as sinks for metals. As a result of several field and laboratory studies indicating that metals in mine drainage can be retained in Sphagnum wetlands (Huntsman et al. 1978, Wieder and Lang 1982, 1984, Kleinmann et al. 1983, Burris et al. 1984, Gerber et al. 1985, Tarleton et al. 1984, Wieder et al. 1985a), there has been an increased interest in the potential use of man-made wetland systems for the treatment of metal-enriched waters, such as those often resulting from coal and metal mining activity (Girts and Kleinmann 1986). Because metals typically do not have a gaseous phase, it is reasonable to assume that, like phosphorus, the capacity for metal retention in wetland systems is finite. However, relatively little effort has focused on developing quantitative estimates of the ultimate long-term capacity for metal retention in man-made wetland systems constructed specifically for mine drainage treatment.

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Accurate estimation of the ultimate capacity for metal retention in man-made wetland systems would be useful from both practical and regulatory standpoints. From a practical point of view, it is difficult to carry out cost/benefit analyses when the ultimate capacity for metal retention in a particular wetland receiving a particular volume and chemistry of mine drainage is unknown. From a regulatory point of view, any consideration of bond release based on constructed wetland systems for mine drainage treatment cannot be objectively assessed until reliable predictions of long-term effectiveness of wetland treatment systems can be made.

In this paper, an upper limit on Fe retention in *Sphagnum* wetlands is estimated by individually considering the biological and chemical processes contributing to Fe retention in wetland ecosystems. Also, different field monitoring schemes are discussed in terms of their potential for assessing the effectiveness of metal retention within man-made wetland systems and their potential for extrapolating the long-term capacity for effective treatment of mine drainage.

UPPER LIMIT FOR Fe RETENTION

Five processes are primarily involved in Fe retention in *Sphagnum* wetlands: uptake and incorporation of Fe by growing *Sphagnum* mosses, the removal of Fe ions from solution by cation exchange, the specific adsorption of Fe onto organic matter, the formation of insoluble Fe oxides, and the formation of insoluble Fe sulfides. Based on our understanding of the biology and chemistry of each process, it is possible to estimate an upper limit for Fe retention in *Sphagnum* wetlands.

As a plant micronutrient, Fe is taken up by growing *Sphagnum*. The highest reported rate of net primary production of *Sphagnum* is 610 $g/m^2/yr$ (Wieder and Lang 1983). The highest reported Fe concentration in field-collected *Sphagnum* plant tissue is 5.8 mg/g (Rodin and Bazilevich 1967). Multiplying these two values gives an estimate of Fe uptake by growing *Sphagnum* of 3.5 $g/m^2/yr$. This estimate is generous not only because we used the highest reported values for both growth and tissue Fe concentration, but also because *Sphagnum* growth may be inhibited by the high Fe concentrations typical of AMD. For example, in a 33 da laboratory study, growth in length of *S. fallax* in solutions containing 100 mg/L Fe was reduced by 32.5% relative to control plants growing in solutions containing 0 mg/L Fe (Kearney 1986).

The binding of Fe^{2+} to negatively charged sites on the peat matrix provides another mechanism for Fe retention. We have quantified Fe retention through cation exchange by placing 5 g of dried peat into replicate flasks, and adding 100 mL of a solution containing either 0, 2, 4, 6, 8, 12, or 16 meq/L of Fe (added as $FeSO_4$; pH of each solution adjusted to 4.0). After 16 hr, the mixtures were filtered and binding of Fe^{2+} with the concomitant release of other cations from exchange sites was calculated (Fig. 1). Using the Langmuir equation, a maximum retention of Fe^{2+} via cation exchange of 204 ueq/g (5.7 mg/g) was estimated.

As with mineral soils (e.g., McLaren and Crawford 1973, Miller et al. 1983), peat can retain Fe by a chelation-like specific binding of the metal cations to sites on the organic matter matrix. Using 0.1 M $Na_4P_2O_7$ extractions (Wieder and Lang 1986), the highest organically bound Fe concentration that we have ever measured in a *Sphagnum* peat sample is 89.3 mg/g. Although little is known about the chemical nature of the binding sites on *Sphagnum* peat, it appears that the specific binding of Fe to organic matter may be a much more important mechanism for Fe retention than cation exchange in peat exposed to mine drainage.

Iron can also be retained in peat by the formation of insoluble Fe oxides. The highest concentrations of amorphous Fe oxide (oxalate extractable Fe) and crystalline Fe oxide (bicarbonate-citrate-dithionite extractable Fe; Wieder and Lang 1986) that we have ever determined in a peat sample are 62.8 and 39.0 mg/g, respectively. These peat samples were collected from Tub Run Bog, West Virginia, a naturally-occurring *Sphagnum*-dominated wetland receiving inputs of acid coal mine drainage from an adjacent abandoned coal surface mine (Wieder and Lang 1982). To what extent the formation of such Fe oxides is abiotic versus biotic is presently not known. However, indigenous populations of both Fe-oxidizing and Mn-oxidizing bacteria have been found in field-collected samples of *Sphagnum* peat (Stone 1984).

Some studies have suggested that bacterial dissimilatory sulfate reduction and the formation of Fe sulfides could play an important role in the removal of Fe from mine drainage (e.g., Tuttle et al. 1969a,b). Although sulfate reduction and the concomitant formation of Fe sulfides does occur in freshwater *Sphagnum* peat (Behr 1985, Behr 1986, Wieder and Lang 1988), there is little evidence that Fe sulfides accumulate to any significant extent in peat exposed to mine drainage (Tarleton et al. 1984, Wieder et al. 1985a, Wieder and Lang 1986). Presumably, the accumulation of Fe sulfides is precluded by their reoxidation, although at present little is known about the process of sulfide oxidation in freshwater wetland peat (Wieder and Lang 1988). Using the Cr^{2+}-reduction technique (Wieder et al. 1985b), the highest concentration of Fe sulfides (actually $H_2S + S^o + FeS_2 +$

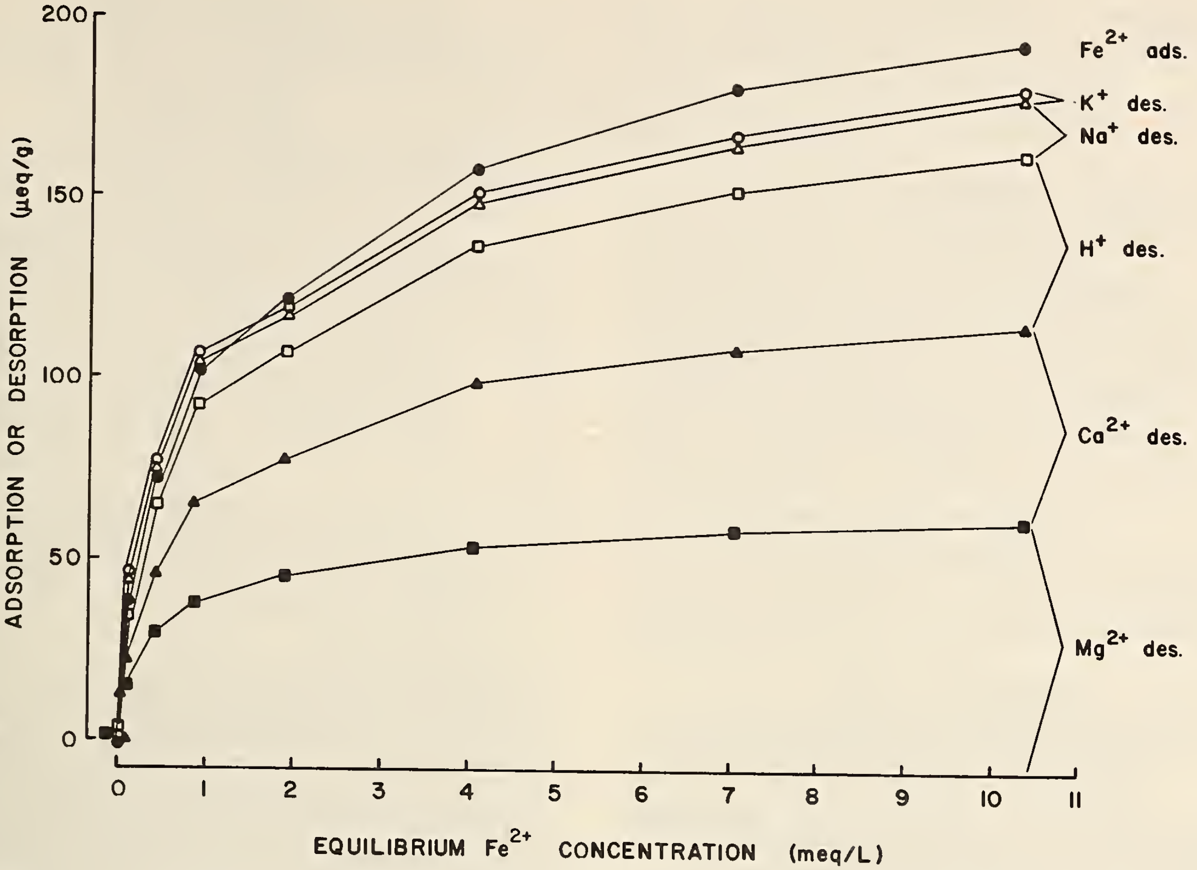

Figure 1. Adsorption of Fe^{2+} onto Sphagnum peat by cation exchange and the corresponding desorption of Mg^{2+}, Ca^{2+}, H^+, Na^+, and K^+.

FeS) that we have ever measured in a single peat sample is 0.7 mg/g Fe.

Assuming that it is possible to obtain maximum Fe retention by each of the above processes, an upper limit on Fe retention in a hypothetical man-made Sphagnum wetland, 40 m by 40 m, 30 cm deep was calculated (Table 1). In making these calculations, a bulk density for Sphagnum peat of 0.1 g/cm was assumed. If such a man-made wetland were exposed to mine drainage with a flow of 4 L/min and a Fe concentration of 100 mg/L (Fe loading rate of 576 g/da), it would take an estimated 44 years until Fe retention by all processes combined would become saturated.

The analysis in Table 1 reveals that incorporation of Fe by growth of Sphagnum and retention by cation exchange and sulfide formation are relatively minor contributors to overall potential Fe retention, as compared to the specific binding of Fe to organic matter and the formation of insoluble Fe oxides. It should be noted, however, that 4 L/min represents a very low flow. If the flow of mine drainage were 40 L/min (still only a moderate flow) and the Fe concentration 200 mg/L, Fe saturation of the wetland would occur in only 2.2 years. The time estimate obtained in Table 1 also assumes that it is possible to obtain the maximum Fe retention by each of the processes involved. In peat samples that have been subjected to mine drainage, either in the field or in the laboratory, rarely have we observed the maximum saturation of Fe retention by all of the processes in Table 1 (Tarleton et al. 1984, Wieder et al. 1985a, Wieder and Lang 1986). To place the estimate of the maximum potential Fe accumulation in Sphagnum peat in some perspective, an Fe concentration of 5,757 g/m^2 (Table 1) is equivalent to an Fe concentration of 19% of the dry mass!

The approach used in Table 1 has provided an estimate of the ultimate capacity for Fe retention in a man-made Sphagnum wetland exposed to mine drainage. However, data from field situations in which wetlands have been constructed specifically for mine drainage treatment are also needed. In the remainder of this paper, we discuss the relative merits and drawbacks of different monitoring schemes for assessing the effectiveness of wetland systems constructed for mine drainage treatment.

Table 1. Maximum Fe retention in a hypothetical man-made *Sphagnum* wetland.

Process	Maximum Retention (g/m)	Days to Reach Saturation
Growth of *Sphagnum*	3.5	9.7
Cation exchange	171	475
Adsorption onto organic matter	2508	6967
Formation of amorphous Fe oxides	1884	5233
Formation of crystalline Fe oxides	1170	3250
Formation of Fe sulfides	21	59
Total	5757	15994 = 44 yr

MONITORING SCHEME 1

Periodic Measurement of Inflow and Outflow Water Chemistry

The most commonly employed monitoring scheme entails the periodic measurement of inflow and outflow water chemistry. Obviously, outflow water chemistry is of particular interest, since if a wetland has been constructed for the treatment of coal mine drainage on an active mine, Federal and/or State water quality criteria must be met for water discharged from the mine site. However, outflow water chemistry alone provides little if any information about the effectiveness of the wetland for metal retention.

Often, both inflow and outflow water chemistry are determined, and a "treatment efficiency," defined as $(C_i - C_o)/C_i$, where C_i and C_o are the inflow and outflow concentrations, respectively, for a particular metal is calculated (Girts and Kleinmann 1986, Girts et al. 1987). Although this index of wetland performance is intuitively satisfying, site hydrology and frequency of sampling are two factors that must be taken into consideration when interpreting treatment efficiency data.

The observation that metal concentrations in outflow water are lower than those in inflow water is suggestive that the wetland is retaining metals, but is by no means sufficient evidence. Possible dilution of influent mine drainage by unmeasured, and perhaps not readily discernible, sources of "good quality" seepage water (i.e., with relatively low metal concentrations) could produce inflated estimates of treatment efficiency within the wetland. Thus, the index of treatment efficiency is valid only in hydrologically tight wetlands where the inflowing mine drainage represents the only significant source of water and metals and where all of the water exits the wetland either at the location of the outflow water sample or via evapotranspiration. Most man-made wetlands are situated in topographically low-lying areas, often where seeps are common. Moreover, when heavy equipment is used during construction of man-made wetlands, seepage may be enhanced as a result of soil excavation. Thus, it is likely that in many instances the condition of hydrologic tightness in a man-made wetland is not satisfied.

The calculation of treatment efficiency based on mean metal concentrations averaged over long periods of sampling may mask seasonal patterns (i.e., winter versus summer) or more short-term patterns such as those that may be associated with major rain events. For example, it is possible that a wetland may be actively retaining metals during relatively dry periods (e.g., by the formation of metal oxides during periods of low water table), but that accumulated metal oxide flocs are flushed downstream during major rain events (cf. Lang and Wieder 1985). Thus, the nature of the data base must be taken into consideration when interpreting treatment efficiencies.

Despite the potential problems in interpreting data resulting from the periodic measurement of inflow and outflow chemistry in a man-made wetland, long-term changes in treatment efficiency (i.e., a progressive decrease in treatment over several years) at a particular site may be informative, assuming that the hydrologic conditions remain relatively constant over the entire sampling period. Advantages to this monitoring scheme are the minimal effort and minimal expense required.

MONITORING SCHEME 2

Periodic Measurement of Inflow and Outflow Water Chemistry with Measurement of Inflow and Outflow Water Fluxes

The monitoring scheme described above can be improved upon substantially by the installation of instrumentation to measure influent and effluent water fluxes since both water and chemical budgets can be quantitatively estimated for a man-made wetland system. If the estimated quantity of water leaving a wetland is less than the quantity entering, and if the difference is comparable to regional estimates of evapotranspiration, then dilution of the mine drainage by good quality seepage water is probably not occurring at the site.

Once a hydrologic budget is calculated and determined to be reasonable, then periodic measurements of metal concentrations in inflow and outflow waters can be used to construct metal budgets for the wetland. The accuracy of the estimates of net retention/release of a particular metal obtained from a metal input/output budget is improved as the frequency of sampling water for chemical analysis increases. Metal budgets can be used to evaluate changes in the metal retention efficiency of a wetland either on a short-term basis (i.e. during and following a rain event), seasonally, or on an annual basis. If a trend of decreasing metal retention is obtained over time, extrapolation may provide a quantitative way of estimating the long-term capacity of a particular wetland for retaining a particular metal (cf. Richardson 1985).

Although the construction of water and metal budgets for a wetland provides a much better indicator of metal retention efficiency than the "treatment efficiency" index discussed under Scheme 1, the associated cost increase can be substantial. Continuous monitoring of water flows requires careful and costly setup, as well as a considerable time commitment involved in subsequent maintenance and data reduction.

MONITORING SCHEME 3

Periodic Measurement of Inflow and Outflow Water Chemistry with Measurement of Inflow and Outflow Water Fluxes and Periodic Analysis of the Wetland Substrate

While Scheme 2 represents a considerable improvement over Scheme 1 with respect to being able to evaluate metal removal efficiency and to project the long-term capacity of the wetland to retain metals, a potential problem with Scheme 2 is that the metal budgets are constructed using occasional measurement of metal concentrations in inflow and outflow waters. Thus, if the flushing of metals from a wetland during major rain events is indeed considerable, but rain event sampling is not carried out, the efflux of metals from the wetland will be underestimated in the metal budget calculation and wetland efficiency for metal retention will be overestimated.

Periodic determination of metal concentration in the wetland substrate can be used to verify metal accumulation determined from the metal budget calculations. Accurate estimation of metal accumulation in the substrate depends on analyzing a sufficient number of substrate samples. In addition, if the substrate samples are dried and ground prior to chemical analysis, values for water content and bulk density of the substrate must be obtained in order to estimate metal accumulation within the entire wetland. Besides providing verification for water budget calculations, trends indicating increases in metal concentrations in the substrate over time can also be used to extrapolate long-term capacity for metal retention in a wetland.

In comparison to Scheme 2, this approach to monitoring a man-made wetland involves the additional expense of collection and analysis of sediment samples.

DISCUSSION

It has been suggested that man-made wetlands may offer a low-cost approach to mine drainage treatment (Wieder and Lang 1982, Kleinmann et al. 1983, Girts and Kleinmann 1986). However, based on the analysis in Table 1, it appears that wetland treatment of mine drainage has a limited potential. Although Table 1 focuses on Fe retention in *Sphagnum* wetlands, it is likely that, at least qualitatively, the findings apply to other metals and to other types of wetland systems as well. The construction of wetlands may be attractive for the treatment of seeps with low flow volumes, but as the flow of the mine drainage increases and/or the metal concentrations in the mine drainage increase, the effective life-time of a man-made wetland will decrease.

In response to the increased interest in using man-made wetlands for mine drainage treatment, the U.S. Office of Surface Mining, Reclamation and Enforcement has adopted the policy that man-made wetlands may be used on active mine sites as long as a fully operational water treatment capability is in place and operational downslope from the wetland and within the permit area. A second part of that policy is that given the present state of knowledge, bonds should not be released based on the installation of man-made wetlands to treat mine drainage.

From a purely practical point of view, if the immediate goal of using a man-made wetland for mine drainage treatment is to meet Federal and/or State water quality criteria, perhaps the single most important measurement is water quality at the outflow from the wetland. Such minimal sampling, however, will provide no insight into either the efficiency of the wetland for metal retention or, and perhaps more importantly, the long-term capacity of the wetland for metal retention. Until field monitoring schemes and/or other approaches allow for the quantitative, reliable estimation of the long-term capacity for metal retention within a wetland given a particular volume and chemistry of water, the environmental and economic potentials of wetland treatment of coal mine drainage remain difficult to quantitatively assess.

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IMPLICATIONS OF SULFATE-REDUCTION AND PYRITE FORMATION PROCESSES FOR WATER QUALITY IN A CONSTRUCTED WETLAND: PRELIMINARY OBSERVATIONS[1]

By Robert S. Hedin, David M. Hyman and Richard W. Hammack[2]

Abstract--Preliminary observations of water chemistry in a recently constructed Typha wetland indicate significant improvements in water quality in areas where reduction processes are occurring. Where the organic substrate was black and loose, sulfate concentrations were 16-59 pct less than inflow, iron concentrations were 52-98 pct lower, and pH was 2-3 units higher. Ninety-six pct of the iron in these areas was in the reduced, ferrous form. Where the organic substrate was blanketed with orange iron oxyhydroxides, water chemistry was similar to inflow, and dissolved iron was predominantly in the oxidized, ferric form. Analyses of the organic substrate (mushroom compost) showed an enrichment of elemental sulfur in all samples. One substrate sample, collected 15 cm beneath the surface, contained both elemental sulfur and pyrite. Removal of iron from acid mine drainage (AMD) through pyrite formation and storage in anoxic sediments may be preferable to removal by oxidation and hydrolysis because of pyrite's density, negligible solubility in acid water, and placement in the substrate. Researchers should consider designs that would emphasize movement of AMD through organic-rich, anoxic substrates and thus maximize sulfate reduction and pyrite-forming processes.

INTRODUCTION

Dissimilatory sulfate reduction and pyrite formation are biogeochemical processes that conceptually can contribute significantly to the effectiveness of constructed wetlands in treating acid mine drainage (AMD). In the absence of oxygen, bacteria such as Desulfovibrio oxidize organic matter using sulfate as an electron acceptor and subsequently reducing it to hydrogen sulfide (see reactions in Table 1). When released into the water column, hydrogen sulfide either bubbles away as a gas (the common rotten eggs odor of many wetlands) or is retained in the wetland as sulfides, polysulfides, elemental sulfur, iron monosulfides (FeS) and pyrite (FeS_2). The reduction process produces alkalinity, which decreases acidity and raises pH. Formation of metal sulfides removes iron from solution. Because such changes in water chemistry are the primary goals of most AMD treatment systems, a better understanding of reducing reactions might result in significant improvements in the constructed wetland technology.

In this paper we report preliminary results of water and substrate analyses from a recently constructed wetland that, in areas, has operating sulfate reduction and pyrite formation processes. We show the dramatic differences in water chemistry that exist in these areas, as compared to inflow water or nearby oxic zones. We also show that the organic substrate is accumulating reduced sulfur compounds and, at depth, pyrite is forming.

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Sulfate Reduction

Sulfate reduction is a common anaerobic, microbial decomposition process. Its occurrence is dependent on the presence of sulfate and suitable organic matter in an anoxic, aquatic environment. In marine systems sulfate levels are very high, and sulfate reduction is only limited by the presence of suitable organic matter in anoxic sediments (Berner 1984). In most freshwater systems, sulfate reduction is limited by very low sulfate concentrations and microbially-mediated methanogensis is the more important anaerobic, decomposition process (Cappenberg 1974, Lovley and Klug 1986). Because the formation of iron sulfides is primarily dependent on the presence of reduced sulfur, freshwater sediments typically have very low pyrite levels (Berner and Raiswell 1983).

Wetlands constructed for the treatment of AMD have none of these limitations. During the first several years of operations, they contain a huge amount of high-quality organic matter. The systems typically consist of at least a thousand cubic meters of fertile, composted organic matter that is spread 15-30 cm deep in a shallow pit, flooded, and overlain by 10-20 cm of slowly flowing AMD water. Aerobic decomposition of the organic matter at the water/substrate interface promotes anoxic conditions within the flooded organic substrates. The acid mine drainage flowing through these wetlands is enriched with dissolved sulfate and iron. Thus, all the conditions for high rates of sulfate reduction and pyrite formation exist.

The expectation that reduction processes could be important in constructed wetlands is not without precedent. Tuttle et al. (1969) studied an AMD-polluted stream in Ohio that flowed through a sawdust dam and was effected by reduction processes within the sawdust pile. Water samples collected below the dam had sulfate concentrations 60 pct lower and iron levels 50 pct less than samples collected above the dam. Herlihy and Mills (1985) and many of their students have studied a reservoir in Virginia that receives AMD from abandoned pyrite mines. Summer sulfate reduction rates in sediments near the AMD inflow are consistently at least a magnitude higher than control areas. Acid volatile sulfide concentrations, which are assumed to represent iron monosulfides, are always a magnitude higher in the AMD impacted sediments than in the control sediments.

Despite these observations, the role of reduction processes in constructed wetlands has received very little attention. Most research has focused on uptake of iron by plants, or microbially-mediated metal oxidation processes (e.g. Kleinmann et al. 1983, Gerber et al. 1985, Wieder and Lang 1986, Kearney and Wieder, elsewhere in these proceedings, Webster et al., elsewhere in these proceedings). In the only published studies that specifically looked for reduced sulfur compounds (and found minor amounts), either the samples were collected from the top 20 cm of peat in a natural Sphagnum wetland (Wieder and Lang 1986) or laboratory mesocosms were only 20 cm deep (Tarleton et al. 1984). Such shallow depths are not conducive to development of the permanent anoxic conditions that are necessary to promote pyrite accumulation.

SITE DESCRIPTION

The wetland monitored in this study is located in Westmoreland County, Pennsylvania about 16 km (10 mi) north of Latrobe. The wetland was constructed in the spring of 1987 to treat drainage from recently strip-mined coal spoils (Figure 1). It is a cattail-dominated (Typha) community growing on a substrate of 15 cm (6 in) of crushed limestone, covered with 45 cm (18 in) of mushroom compost[3]. Water depths over the substrate are 5-20 cm (2-8 in). Baffles were constructed in each cell with bales of hay to promote a serpentine flow path. By September, 1987 a dense stand of cattails had developed. Seepage drains from the reclaimed mine spoils at flows of 40 to 120 L/min (10 to 30 gals/min). It is collected in a shallow pit, which was also filled with substrates and planted with cattails, and then flows 30 m (100 ft) over limestone rip-rap into the wetland.

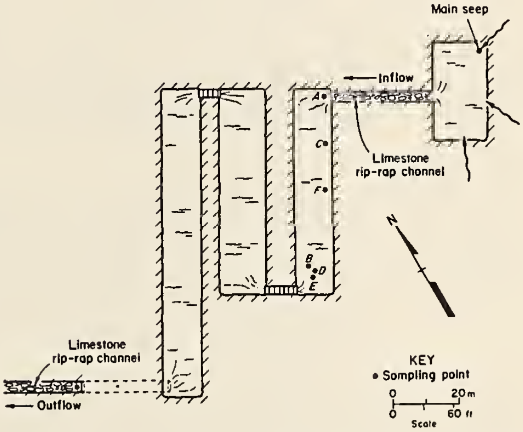

Figure 1.--Plan view of the constructed wetland.

METHODS

The wetland was examined and sampled in autumn of 1987. Chemical measurements were made directly in the field and in Bureau of Mines' laboratories at the Pittsburgh Research Center. Numerous pH determinations were made using a temperature-compensated, field pH meter (Orion Model 230) with a Ross combination electrode. The electrode and meter were calibrated and measurements were subsequently made by placing the probe directly into wetland water. Dissolved oxygen (DO) was measured on October 7 with a portable polarographic sensor and field meter (Extech Model 9070). Because this DO probe could not be completely submerged, measurements reflect DO only to a depth of about 5 cm (2 in) beneath the water surface.

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[3] Mushroom compost, a waste product of local mushroom growers, is produced by aerobically composting a mixture of spoiled hay, agricultural wastes, and animal manure.

Table 1.--Important chemical reactions in anaerobic, sulfate-rich environments

	Reaction description	Reaction	Ref[2]
1.	Sulfate reduction	$SO_4^{2-} + 2CH_2O^* \text{ ---> } H_2S + 2HCO_3^-$	(1)
2.	hydrogen sulfide ionization	$H_2S \text{ ---> } HS^- + H^+$ $HS^- \text{ ---> } S^{2-} + H^+$	(2)
3.	formation of elemental sulfur	$HS^- + 1/2O_2 + H^+ \text{ ---> } S^0 + H_2O$	(2)
4.	polysulfide formation	$HS^- + (x-1)S^0 \text{ ---> } S_x^{2-} + H^+$	(2)
5.	iron monosulfide formation	$Fe^{2+} + HS^- \text{ ---> } FeS + H^+$	(4)
6a.	pyrite formation	$FeS + S^0 \text{ ---> } FeS_2$	(4)
6b.	pyrite formation	$Fe^{2+} + S^0 + H_2S \text{ ---> } FeS_2 + 2H^+$	(3)
6c.	pyrite formation	$Fe^{2+} + S_x^{2-} + HS^- \text{ ---> } FeS_2 + S_x^{2-} + H^+$	(3)

[1] CH_2O represents organic matter.

[2] References are: (1) Berner 1984; (2) Chen and Morris 1972; (3) Altschuler et al. 1983; (4) Berner 1967.

Table 2. Changes in water Quality between the main seep and wetland inflow on October 27, 1987

	pH	Acidity	Sulfate	Fe	Fe^{2+}	Al	Mn	Na	Ca	Mg
main seep	3.04	1000	2125	227	146	49	36	4	188	134
inflow	3.02	909	2075	203	62	51	38	4	209	139

Acidity is mg/L of $CaCO_3$ equivalent; all other values, except pH, are mg/L.

Water samples were collected at various locations (Fig. 1) and analyzed in the laboratory for pH, acidity, sulfate, Fe^{tot}, Fe^{2+}, Mn, Al, Ca, Mg, and Na using standard methods (e.g. Watzlaf 1986). Substrate samples were collected in plastic bottles which were filled to capacity, capped, and refrigerated. In the laboratory, these samples were centrifuged to separate solids from liquid, and the supernatant was either analyzed or discarded. The solids were dried under vacuum and stored under argon. Total sulfur was determined using a LECO SC-32 Sulfur Determinator. Sulfur forms were distinguished using evolved gas analysis (EGA) and X-ray photoelectron spectroscopy (XPS) (Hammack, elsewhere in these proceedings). X-ray diffraction was used to corroborate EGA and XPS results. The acid-soluble metal content of solids was determined by boiling a weighed sample in aqua regia (a mixture of hydrochloric and nitric acids) and measuring the metal concentrations of the acid extract after filtering it through a Whatman No. 42 filter.

RESULTS

When first examined five months after construction, the limestone rip-rap in the ditch preceding the wetland was coated with iron oxyhydroxides and had little effect on drainage chemistry (Tab. 2). On several other occasions we measured the pH of water in the pit and at the inflow and never found substantial differences. The only major change in water chemistry between the main seep and the wetland inflow was partial oxidation of the ferrous iron (Fe^{2+}). Thus, on all sampling dates we have collected wetland inflow samples from the end of the riprap (location A in Fig. 1).

Since September, 1987, the wetland has displayed a variable appearance. In some areas the organic substrate is coated with about 1 cm of an orange precipitate that is sometimes hard and crusted. In other areas the substrate is black and loose. We have visually estimated that black areas represent about 20 pct of the wetland area, while orange areas represent the rest. Occasionally the substrates in black areas are covered with a fine, white precipitate. Many of the black areas are located in stagnant water behind haybales, while orange-colored areas tend to be on the upstream sides of haybales and in the central, main-flow area. Density of living cattails does not appear to be substantially different between the areas.

The dissolved oxygen (DO) concentrations of surface water were lower in black areas than in orange areas (Tab. 3). The highest DO value, 10.1 mg/L or 99% of saturation (water temperature = 13° C, saturation = 10.2 mg/L (Truesdale et al. 1955)), was found overlying an orange area near the inflow. Downstream of the first row of hay bales in the first cell, the DO of surface water in an orange area was 9.0 mg/L. A black area, only 1 meter away, had a surface DO content of 5.0 mg/L. By the time water reached the outflow pipe at the end of the third cell, DO levels were depressed everywhere. However, surface water in black areas still had 1.2-1.9 mg/L lower DO concentrations than nearby orange areas (Tab. 3). Losses of dissolved oxygen were likely due to consumption of oxygen by aerobic decomposition of organic matter at the substrate/water interface, as well as aerobic oxidation of ferric iron by chemical and microbial processes. The lower values in black areas could have resulted from higher oxygen consumption, less mixing with oxygenated water, or both. Nowhere did we find surface water DO levels low enough to be considered anoxic. We suspect, based on sulfur and iron analyses (to be discussed), that anoxic conditions existed several cm beneath the water/organic substrate interface.

Table 3. Dissolved Oxygen Content of Surface Water in Various Environments

Area description	DO (mg/L)
Seep collection pit	8.7
First Cell	
Inflow, after riprap	9.2
Orange area upstream of first haybales	10.1
Orange area downstream of first haybales	9.0
Black area downstream of first haybales	5.0
Third Cell	
Water entering outflow pipe	5.0
Orange area near outflow pipe	5.3
Black area near outflow pipe	3.4
Black area near outflow pipe	4.1

The orange precipitate that coats much of the organic substrate in this wetland was 21% iron (Tab. 5) and appears to be an iron oxyhydroxide that commonly forms when dissolved iron in AMD is oxidized and hydrolyzed. In the first cell, the chemistry of surface water flowing through orange areas was very similar to inflow water. Numerous pH measurements in the first cell (not detailed here) consistently found values only several tenths of a unit higher than the inflow. The chemistry of water collected at the substrate/water interface in an orange area at the end of the first cell is shown in table 4 (sample B). Despite having flowed through 60 m of wetland, the chemistry was quite similar to the inflow (sample A). The only notable chemical changes were a decrease in total iron of 34 mg/L (19 pct of inflow) and an equivalent loss of ferrous iron.

This loss of dissolved ferrous iron, combined with the presence of iron oxyhydroxide precipitates, indicates the predominance of oxidizing reactions in these areas. Because abiotic oxidation of ferrous iron is quite slow at low pH, the changes in Fe^{2+} in orange areas were presumably mediated by iron-oxidizing bacteria. These bacteria may also be involved in the removal of iron from solution as oxyhydroxides (Gerber et al. 1985). The fact that a significant portion of this wetland is covered with iron oxyhydroxides indicates the historic importance of oxidizing reactions to overall iron removal. However, it is also important to note that the current activity of these orange areas appears to be limited. Iron is only slightly decreased, while all other chemical parameters are virtually unchanged.

Areas in which the substrate surface were black had markedly different water chemistry than the inflow, or even orange-colored areas located less than one meter away. These differences are readily seen in table 4 by comparing samples C, D and E to A and B. All three samples were collected from the substrate/water interface in black areas in the first cell (fig. 1). Samples from black areas had dissolved iron concentrations that were much less than samples at the inflow or nearby orange areas. The dissolved iron concentration in sample D was only 3 pct of inflow. Over 95 pct of the dissolved iron that was observed in black areas was in the reduced ferrous form. This contrasted markedly with the inflow sample, which was 40 pct ferrous, and the nearby orange area sample, which was only 27 pct ferrous.

Table 4. Water Chemistry for Samples Collected October 7, 1987

	SAMPLE	CHEMICAL MEASUREMENT									
#	LOCATION	pH	Acidity	Sulfate	Fe	Fe^{2+}	Al	Mn	Na	Ca	Mg
A	Inflow	2.86	872	2050	181	73	50	36	4	194	133
B	Orange area	2.96	777	2000	147	39	47	36	5	223	139
C	Black area	4.75	10	1725	30	28	bd	58	5	404	159
D	Black area	5.39	5	850	3	3	bd	11	6	214	82
E	Black area with white precipitate	4.60	159	1000	87	84	bd	20	4	171	75

Acidity is mg/L of CaCO$_3$ equivalent; all other values, except pH, are mg/L; "bd" is below detection level of instrument (<0.4mg/L).

Table 5. Acid Soluble Metal Content of Substrate Samples Collected at the Water/Substrate Interface on October 7, 1987

#	SAMPLE LOCATION	METAL CONTENT (% OF DRY WEIGHT)					
		Fe	Mn	Al	Ca	Mg	Na
B	Orange Area	21.4	<0.1	<0.1	<0.1	<0.1	<0.1
E	Black Area with white precipitate	0.2	<0.1	9.8	<0.1	<0.1	<0.1

Percentages do not sum to 100% because of carbon, oxygen, hydrogen, sulfur and acid-insoluble metals.

Dissolved aluminum was decreased to undetectable levels (<0.4 mg/L) in all samples from black areas. Sample E represented an attempt to collect a fine white precipitate that covered the black substrate in several areas. Large amounts of black substrate were unavoidably included in the sample. Analysis of the acid-soluble constituents of this material revealed an aluminum content of almost 10 pct (tab. 5). Based on the color and this analysis, it appears that the white precipitate was aluminum hydroxide, which commonly forms when the pH of Al-containing water rises above 3.5. Note that, unlike the substrate sample taken only one meter away in an orange area, iron was a minor component of the substrate solids. Despite the fact that dissolved iron was very low in the black areas, it's loss was not due to precipitation and accumulation on the surface of the organic substrate.

Samples in black areas were much less acidic than the inflow or nearby orange area samples. Additional pH measurements have indicated that the surface water in black areas generally has a pH between 4.0 and 4.5, while the water within the organic substrate often has a pH greater than 6.0. This decreased acidity cannot be entirely attributed to the neutralizing effect of underlying limestone. Two of the three samples had dissolved calcium concentrations very similar to the inflow. Only sample C had higher calcium levels, but the increase over inflow, 5.25 mm/L (millimoles per liter), was not enough to explain the 8.6 mm/L decrease in acidity ($CaCO_3$ equivalents).

Presumably, part of the decreased acidity resulted from sulfate reduction (eq.1, tab. 1). Dissolved sulfate concentrations of samples C, D, and E were lower than samples from both the inflow and orange areas (Tab. 4). Sample D had only 41 pct of the inflow sulfate concentration. When disturbed, sediments in virtually every part of the wetland released considerable emissions of gas bubbles and the characteristic odor of hydrogen sulfide was evident. This combination hydrogen sulfide production and decreased dissolved sulfate and acidity is very strong evidence for sulfate reduction.

Once released into the water column by sulfate-reducing bacteria, H_2S has several possible fates. In acidic water, ionization is low (Eq. 2 in Tab. 1) and H_2S can escape from the wetland as a gas. Under alkaline conditions, ionization potentially results in significant concentrations of both HS^- and $S2^-$. These dissolved sulfides can be oxidized to elemental sulfur by oxygen (Eq. 3) or react with ferrous iron to form monosulfides or pyrite (Eq. 5 and 6c, respectively). Secondary reactions of elemental sulfur can result in polysulfides (Eq. 4) and pyrite (Eq. 6a and 6b). All of these products precipitate and thus remove iron and sulfide from solution. Iron monosulfides oxidize very quickly in aerobic environments and decompose in acidic solutions to ferrous iron and hydrogen sulfide (reverse of eq. 2 and eq. 5). Pyrite and elemental sulfur also oxidize to sulfate if oxic conditions develop, but neither is soluble in the sulfuric acid that gives AMD its acid character.

Currently, judgments about the relative importance of each of these sulfur-containing compounds in this constructed wetland cannot be made. However, it is certain that sulfide reduction in excess of that required for iron sulfide formation is occurring. Water samples in black areas had, on average, 2.5 mm/L (millimoles per liter) less iron than inflow water. If all this iron was removed by formation of monosulfides and pyrite, 2.5-5.0 mm/L of sulfide would have been required. Sulfate concentrations in the black areas averaged 9.0 mm/L less than inflow samples. Thus, at least 4.0 mm/L of reduced sulfur must have been either released as gaseous H_2S, or retained in the wetland in a reduced from not associated with iron.

Except when we disturbed the sediments by walking in the wetland, we noticed little odor of hydrogen sulfide. This observation may be explained by the alkaline conditions that exist in the organic substrates and which should cause ionization of H_2S to the dissolved sulfide forms. If losses of sulfide as H_2S are not major, then retention and accumulation of reduced sulfur in the organic substrates must be occurring. We evaluated this hypothesis by analyzing samples of the organic substrate for sulfur content (LECO sulfur analyzer) and sulfur form (evolved gas analysis). Mushroom compost in its original form has a sulfur content of about 1.5 pct, most of which is in the sulfate form. All substrate samples collected from this wetland have contained more than 2.0% sulfur, and we have measured total sulfur contents as high as 10.2 pct for black particulates filtered from wetland water samples. The organic substrate filtered from sample D was 3.2 pct sulfur. Evolved gas analysis (Fig. 2) of this sample showed that most of the sulfur was elemental with subordinate

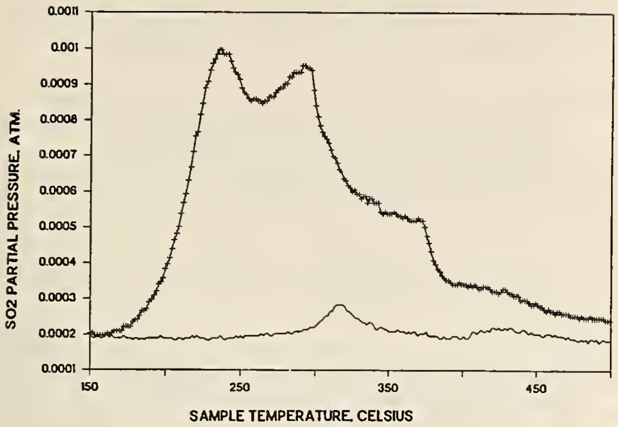

Figure 2.--Evolved gas analyses of fresh mushroom compost (lower line) and substrate samples collected from the constructed wetland (upper line). The wetland sample was collected from the substrate surface at location D. The plotted lines indicate evolution of SO_2 as the samples were heated from 50°C to 1000°C (only the 150-500°C range is shown). SO_2 evolution temperature ranges for important sulfur forms are: reduced and elemental sulfur, 150-300°C; carbon-bonded sulfur, 300-350°C; pyritic sulfur, 375-425°C; sulfate, 800-900°C. The fresh compost sample had a very large peak in the sulfate range that is not shown.

amounts of organic sulfur that co-evolved with aliphatic hydrocarbons. The presence of elemental sulfur was confirmed with XPS and X-ray diffraction. Elemental sulfur was not present in the original compost material (Fig. 2). Pyrite, which is indicated by peaks between 380° C and 420° C, was not found. This was not unexpected because the samples were collected from the surface of substrates overlain by shallow oxygenated water. Authigenic pyrite (pyrite formed in place, not transported) is not stable in such an oxidizing environment.

Based on the high iron and reduced sulfur concentrations observed in the wetland, pyrite would be expected to form in anaerobic areas. We tested this prediction by collecting one sample from 15-20 cm deep in the organic substrate (location F in Figure 1). The sampling area was a black pool, and the pH of disturbed water after sampling was greater than 6.0. Evolved gas analysis of the solid organic material revealed the presence of large amounts of elemental sulfur, as well as a smaller amount of pyritic sulfur (Figure 3). The identification of pyrite was confirmed with X-ray diffraction analysis. Although we have not performed experiments yet to ascertain that this pyrite is authigenic (versus being washed in from surrounding spoils), we believe that the environmental conditions, as well as the pyrite's location in the organic substrate argue strongly for an authigenic origin.

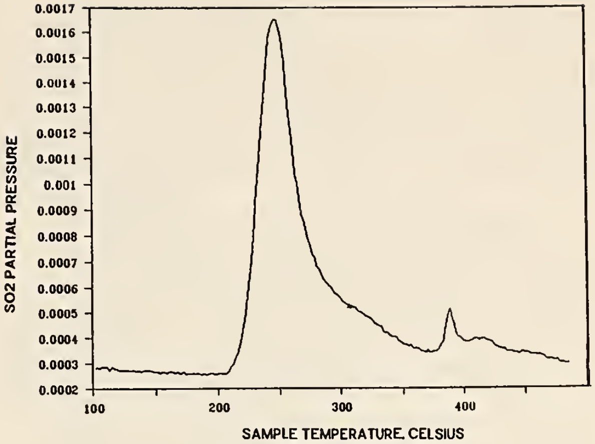

Figure 3.--Evolved gas analysis of organic substrate collected 15-20 cm deep in the constructed wetland. The peak at 390°C indicates pyrite, while the larger one at 250°C is elemental sulfur.

DISCUSSION

Many biogeochemical processes interact to cause the amelioration of AMD chemistry as it flows through a natural or constructed wetland. Sulfate reduction and pyrite formation, though often cited as the desirable, ultimate sink for iron removal in constructed wetlands, have received little research attention. The results in this paper illustrate the dramatic chemical changes associated with reducing zones in a newly constructed wetland.

These processes also would appear to have important advantages over other mechanisms of AMD amelioration. Unlike oxidation processes, which produce acidity, sulfate reduction produces alkalinity (Eq. 1 in Tab. 1). Sulfate reduction and pyrite formation processes are not constrained by accumulation limits or toxic effects. Hydrogen sulfide is a waste product of dissimilatory sulfate-reducing bacteria that is expelled, not accumulated. Pyrite formation occurs for solubility reasons (Howarth 1979) or because of chemical transformations in existing inorganic sulfur compounds (Berner 1984, Altschuler et al. 1983). These processes contrast with bioaccumulation or chelation/adsorption processes. Many wetland plants can remove metals from solution, however, accumulation is generally limited by toxicity factors (Kearney and Wieder, elsewhere in these proceedings). Organic matter, such as peat, has a well documented tendency to accumulate metals, but it is constrained by adsorption limitations (Wieder and Lang 1986).

Pyrite may also be preferable over the iron oxyhydroxides that form by oxidation and hydrolysis reactions for several reasons. It accumulates within the organic substrates and is less likely than surface deposits of iron oxyhydroxides to be flushed out of the wetland during storm events. As long as pyrite stays in a reducing environment, it is insoluble in AMD. Iron oxyhydroxides can be resolubilized if the drainage becomes more acidic. Pyrite is a quite dense compound whose accumulation would not be expected to change flow or mixing regimes. Iron oxyhydroxides are not as dense, and by accumulating on the surface can fill the wetland and deleteriously effect flow and mixing patterns.

Presently we are unable to estimate the importance of reducing reactions as compared to oxidizing reactions and plant uptake in this wetland. However, if reduction processes are to be maximized in constructed wetlands, it is likely that designs must be reconsidered. Currently, most constructed wetlands have very high surface:volume ratios which maximize aeration of water. The result is surface conditions that are conducive for oxidation and hydrolysis reactions and, potentially, the formation of voluminous iron oxyhydroxides on top of the organic substrate. This blanket must interfere with mixing of surface and subsurface water. Over time, oxidation and reduction processes likely become more disconnected, and the possibility exists that the importance of reducing reactions will decrease. Design features that maximized flow through anaerobic environments might be more effective in the long term. For example, if inflow pipes were positioned at the base of the wetland, water would be forced to rise through anoxic organic matter, presumably stimulating sulfate reduction and pyrite formation. When water reached the surface, it would then be "polished" by oxidation and hydrolysis reactions. This bottom flow system has natural analogies in the New Jersey Pine Barrens where sulfate entering Sphagnum wetlands in the groundwater is removed by reduction reactions before it reaches the surface (Spratt et al. 1987).

CONCLUSIONS

Reducing environments represent major iron and sulfur sinks that are not being exploited in most wetlands constructed to treat AMD. Compared to water in oxidized zones of this wetland, water in reducing zones has substantially lower concentrations of sulfate, iron, and acidity, while organic substrates are enriched with elemental sulfur and, at depth, are accumulating pyrite. However, these conditions do not exist throughout the wetland, and a considerable flow of water is through oxygenated, surface channels which do not markedly change water chemistry. Wetland builders should consider design features that increase flow through reducing environments, while researchers must determine what factors effect the rates of sulfate reduction and pyrite formation in these wetlands.

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AN EVALUATION OF SUBSTRATE TYPES IN CONSTRUCTED WETLANDS ACID DRAINAGE TREATMENT SYSTEMS

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Abstract--Many wetlands for acid drainage treatment have been constructed by the coal and utility industries with limited information on design and operating criteria. To investigate important components (substrates, vegetation, microbes) in wetlands treatment systems, the Tennessee Valley Authority (TVA) initiated experiments at the Acid Drainage Wetlands Research Facility, Jackson County, Alabama, in September 1986. All substrates (6) provided significant treatment of dissolved iron, suspended solids, and pH. Acid wetland soil was initially more efficient but differences between substrates became insignificant by fall. Only limited manganese removal occurred. The pronounced pattern of removal efficiency improvement, common to all substrate types, suggested that the plant-soil-microbial complex important to acid drainage treatment developed within all tested substrates within one year. Treatment differences between substrates were inadequate to justify added costs of deliberately installing a specific substrate in operating systems; slightly better performance of acid wetland soil supported protecting existing wetlands at construction sites.

INTRODUCTION

Acid water drainage ($pH<6$, $Fe>4$, $Mn>2$), from coal mining, processing, transporting, storage, and burning lowers water quality, impacts aquatic biota, and jeopardizes drinking water supplies throughout the eastern United States. Conventional treatment technology consists of grading and recontouring to reduce or divert flows and addition of alkaline solutions to elevate pH levels and chemically precipitate metallic ions. Land reforming is almost prohibitively expensive, and chemical treatment is not only expensive but often requires a long-term maintenance and operational commitment. Constructed wetlands appear to offer an inexpensive, self-maintaining, long-term solution that may be applicable to small or large flow acid discharges (Brodie et al. 1986, 1987). In addition to others in the coal and utility industry, the Tennessee Valley Authority (TVA) has established

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11 wetland treatment systems at coal mines, coal preparation plants, and coal-fired plants (Brodie et al 1988).

Several investigations have suggested or demonstrated the effectiveness of wetlands in removing acidity, sulfate, iron, manganese, and other pollutants from acid mine drainage (Holm 1983, Pesavento 1984, Weider et al. 1984, Brodie et al. 1987). Some have described failures of demonstration wetlands to achieve desired results (Pesavento 1984, Weider et al. 1985).

Laboratory studies have explored design and operational parameters of wetlands for acid mine drainage treatment (Tarleton et al. 1984, Gerber et al. 1985). Little work has been done on pollutant removal mechanisms of wetlands for mine drainage treatment. Physical/chemical mechanisms may be important, but vegetative and microbiological mechanisms are thought to be the major factors in pollutant removal. Results of various treatment systems have ranged from poor to excellent, and more importantly, few systems have been studied over long time periods (Pesavento 1984, Weider et al. 1984). Competitive advantages of man-made wetlands over chemical treatment are based not only upon short-term economics but upon internal maintenance attributes of wetlands systems that suggest long-term independent functioning of stabilized systems.

TVA's Acid Drainage Wetlands Research Facility (ADWRF) was established for controlled, pilot-scale experiments at an active seep to investigate optimal size, type, and operational longevity of wetlands systems for removing various pollutants from acid drainage. Initiated in September 1986, the first phase is designed to identify most efficient substrate type(s). Future studies will compare removal efficiencies of different wetlands macrophytes and identify important microbial populations (bacteria, fungi, algae, and protozoa) and optimal environmental conditions for water quality improvement.

METHODS

In August 1986, a series of cells, piping, and associated hardware comprising the Acid Drainage Wetlands Research Facility, was assembled at TVA's Fabius Coal Mine Site, Jackson County, Alabama. Each of the 20 cells consisted of a buried, half-round, fiberglass culvert 6.3 m (20 ft) long and 1.1 m (42 in) in diameter (Figure 1). An unlined pond in spoil material

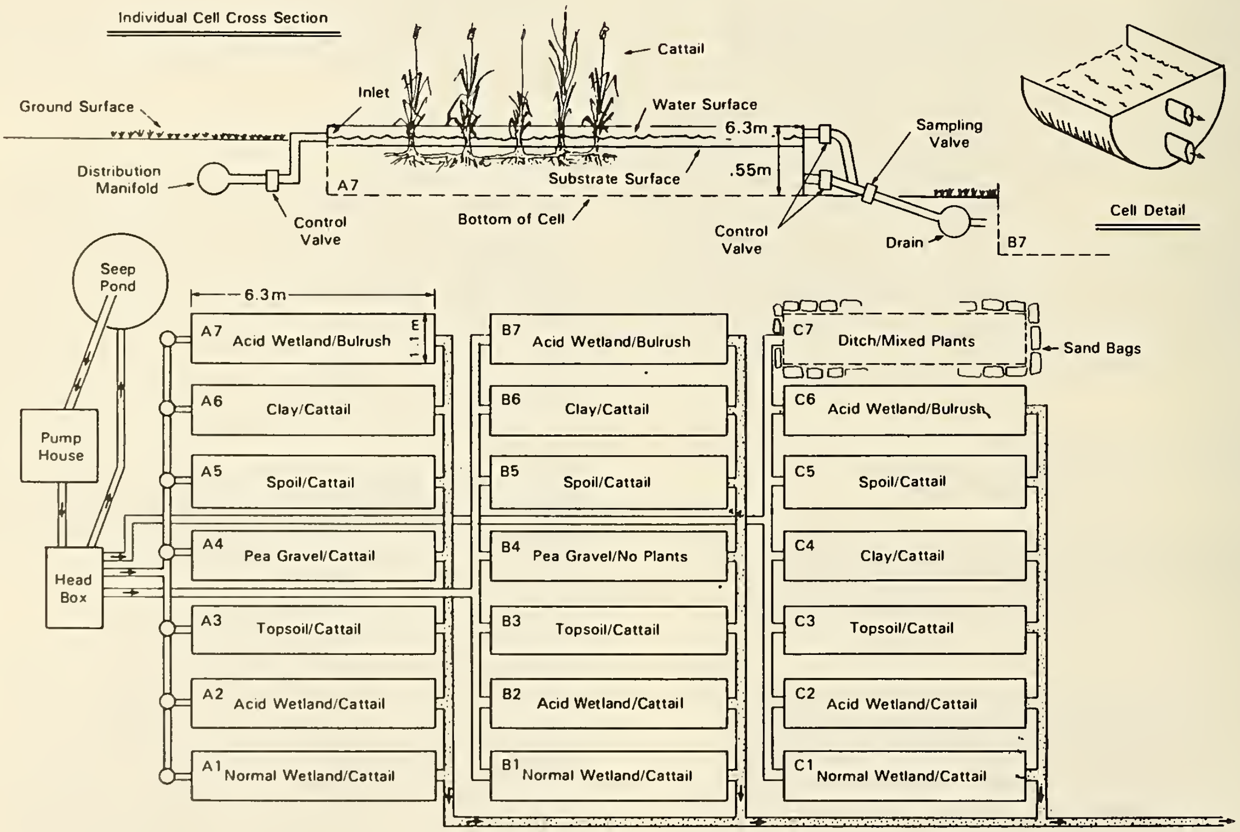
Individual Cell Cross Section
Cattail
Inlet
Ground Surface
Water Surface
6.3m
Sampling Valve
Distribution Manifold
.55m
Substrate Surface
A7
Control Valve
Bottom of Cell
Control Valve
Drain
B7
Cell Detail
Seep Pond
6.3m
A7 Acid Wetland/Bulrush
1.1m
B7 Acid Wetland/Bulrush
C7 Ditch/Mixed Plants
Sand Bags
A6 Clay/Cattail
B6 Clay/Cattail
C6 Acid Wetland/Bulrush
Pump House
A5 Spoil/Cattail
B5 Spoil/Cattail
C5 Spoil/Cattail
A4 Pea Gravel/Cattail
B4 Pea Gravel/No Plants
C4 Clay/Cattail
Head Box
A3 Topsoil/Cattail
B3 Topsoil/Cattail
C3 Topsoil/Cattail
A2 Acid Wetland/Cattail
B2 Acid Wetland/Cattail
C2 Acid Wetland/Cattail
A1 Normal Wetland/Cattail
B1 Normal Wetland/Cattail
C1 Normal Wetland/Cattail

Figure 1. TVA's Acid Drainage Wetlands Research Facility, Jackson County, Alabama - Phase 1 Experiment comparing treatment among substrate types.

was planted with marsh/wet meadow vegetation. Pond and pea gravel cells served as controls.

Water from a mine seep was pumped into a head box and gravity discharged into each cell. A polyvinylchloride pipe collection system discharged into a field scale wetlands treatment system and thence to a stream. Appropriate valving provided flow control to each cell. Seep water had a pH of 5.9 s.u., with 37 mg/L iron, and 16 mg/L manganese.

Substrates

Clay was obtained from the B soil horizon at an undisturbed site near the facility. Mine spoil was obtained on site. Pea-gravel was purchased from a river gravel operation. Topsoil consisted of soil from the A horizon from nearby agricultural fields. Acid wetland consisted of substrate from a natural wetland below an acid seep nearby. Natural wetland consisted of substrate from a nearby natural wetland without acid drainage.

Samples of each substrate type (except topsoil) were analyzed for standard soil composition and chemistry parameters (Table 1). After planting, ten times the desired level of 0.32 kg of 6-12-12 fertilizer was inadvertently placed in each cell resulting in an equivalent rate of 4638 kg/ha (4097 lb/acre).

Vegetation

Initial evaluations (1987-1989) were designed to test cattail (Typha latifolia) with bulrush (Scirpus cyperinus) planted in three cells. Planting material was obtained from nearby wetlands unimpacted by mine drainage. Vegetative material was washed to remove soil, cut to standard stem length of 30 cm, and weighed before planting.

Fifty-seven cattail, average total weight of 6,132 g, were planted on 30 cm centers in three rows of 19 plants in 16 cells on 2 September 1986. Three cells were similarly planted to bulrush, average total weight of 10,639 g, on 4 September. Stem densities and heights were periodically measured throughout the study.

Monitoring

Relatively high flow rates to each cell (1.0 L/min) were established on 18 September 1986 then reduced to 0.5 L/min on 20 December 1986 to accelerate development of differential treatment results. Individual cell flow rates were measured, recorded, and adjusted daily.

Weekly (29 September - 5 November 1986) or twice monthly (after 5 Nov.) inflow water samples, obtained from the manifolds, and outflow samples from the

Table 1. Composition of five substrate types tested at the Fabius Acid Drainage Wetlands Research Facility, Jackson County, Alabama.

	Substrate Types				
Soil Parameters	Natural Wetland	Acid Wetland	Clay	Mine Spoil	Pea Gravel
Organic matter (%)	0.6	0.9	0.5	0.1	1.3
Phosphorus (mg/L)	5.0	6.0	2.0	3.0	1.0
Potassium (mg/L)	94.0	98.0	72.0	67.0	1.0
Magnesium (mg/L)	114.0	80.0	29.0	37.0	1.0
Calcium (mg/L)	650.0	290.0	40.0	20.0	4.0
Sodium (mg/L)	11.0	17.0	9.0	10.0	4.0
pH (mg/L)	7.0	4.4	5.1	4.8	5.7
Nitrate (mg/L)	4.0	4.0	4.0	6.0	1.0
Sulfur (mg/L)	30.0	384.0	41.0	131.0	26.0
Zinc (mg/L)	2.4	7.0	0.9	2.1	0.3
Manganese (mg/L)	122.0	45.0	9.0	6.0	1.0
Iron (mg/L)	94.0	138.0	20.0	8.0	1.0

upper level of each cell were analyzed for pH, temperature, dissolved oxygen, conductivity, total suspended solids (TSS), oxidation-reduction potential, total and dissolved iron (Fe), total and dissolved manganese (Mn), ferrous iron, aluminum, and sulfate. Sample collection and analysis by the TVA laboratory followed standard procedures (US EPA 1979). A two-way analysis of variance (ANOVA) with a Ryan-Einot-Gabriel-Welsch multiple F-test and paired t-tests (SAS 1985) were used in data analysis.

DISCUSSION AND CONCLUSIONS

Since these results represented only the first year of operation of the ADWRF, the statistical analyses were limited to those parameters most important to operational permit discharge limits, i.e., pH, dissolved Fe and Mn, and TSS for the period 14 Jan to 9 Sept 1987.

All substrate types significantly reduced dissolved Fe and TSS and increased pH levels (table 2). Effluent concentrations of dissolved Fe ranged from 4.8 mg/L (acid wetland/cattail) to 7.2 mg/L (topsoil/cattail) (table 3). Total suspended solids in cell effluents ranged from 13.9 mg/L (acid wetland/cattail) to 14.5 mg/L (natural wetland/cattail). Variation in effluent pH values was lower, ranging from 6.2 s.u. (natural acid wetland/cattail) to 6.4 s.u. (topsoil/cattail). Effluent values for dissolved Mn, ranging from

Table 2. Comparisons of influent-effluent concentrations of Fe, Mn, TSS, and pH between 6 replicated substrates from Jan 14-Sept 9, 1987, at the Fabius Acid Drainage Wetlands Research Facility, Jackson County, Alabama (paired t-test, 0.05, SAS, 1985).

Substrate/Vegetation	N	Mean Effluent Concentration (mg/L)	Prob>'t'
	Influent 32.3 mg/l		Dissolved Iron
Topsoil/Cattail	57	7.2	<0.0001
Natural Wetland/Cattail	57	6.1	<0.0001
Clay/Cattail	57	5.6	<0.0001
Acid Wetland/Bulrush	57	5.4	<0.0001
Mine Spoil/Cattail	57	5.3	<0.0001
Acid Wetland/Cattail	57	4.8	<0.0001
	Influent 14.8 mg/l		Dissolved Manganese
Natural Wetland/Cattail	57	14.5	0.254
Clay/Cattail	57	14.3	0.007
Mine Spoil/Cattail	57	14.3	0.006
Topsoil/Cattail	57	14.2	0.006
Acid Wetland/Bulrush	57	14.1	0.038
Acid Wetland/Cattail	57	13.9	0.076
	Influent 32.1 mg/l		Total Suspended Solids*
Topsoil/Cattail	55	16.6	0.008
Clay/Cattail	55	13.6	0.004
Acid Wetland/Cattail	55	12.2	0.001
Mine Spoil/Cattail	55	12.1	0.0006
Natural Wetland/Cattail	55	12.1	0.002
Acid Wetland/Bulrush	55	11.8	0.001
	Influent 5.9 s.u.		pH**
Topsoil/Cattail	56	6.4	0.0001
Acid Wetland/Bulrush	52	6.3	0.0001
Clay/Cattail	54	6.3	0.0001
Mine Spoil/Cattail	53	6.3	0.0001
Natural Wetland/Cattail	54	6.2	0.0001
Acid Wetland/Cattail	53	6.2	0.0001

*Two influent (and corresponding effluent) values over 400 mg/l were excluded from the analysis.

**pH values over 7.5 were excluded from the analysis.

Table 3. Effect of substrate type on effluent concentrations of dissolved Fe and Mn, TSS, and pH from Jan 14-Sept 9, 1987, at the Fabius Acid Drainage Wetlands Research Facility, Jackson County, Alabama (multiple F test, SAS, 1985). Mean effluent values connected by a continuous line are not significantly different.

	Mean Effluent Concentration (mg/L)	N	Wetland Type
Dissolved Iron (mg/l)	5.5	52	Topsoil/Cattail
	5.2	54	Clay/Cattail
	5.1	53	Natural Wetland/Cattail
	4.8	54	Mine Spoil/Cattail
	4.7	54	Acid Wetland/Bulrush
	4.6	53	Acid Wetland/Cattail
Dissolved Manganese (mg/l)	14.3	53	Natural Wetland/Cattail
	14.2	54	Mine Spoil/Cattail
	14.1	54	Clay/Cattail
	14.0	52	Topsoil/Cattail
	14.0	53	Acid Wetland/Cattail
	13.9	54	Acid Wetland/Bulrush
Total Suspended Solids (mg/l)	13.7	52	Topsoil/Cattail
	11.8	54	Clay/Cattail
	11.2	53	Acid Wetland/Cattail
	10.7	54	Mine Spoil/Cattail
	10.2	53	Natural Wetland/Cattail
	10.0	54	Acid Wetland/Bulrush
pH (standard units)	6.4	51	Topsoil/Cattail
	6.3	51	Clay/Cattail
	6.3	49	Acid Wetland/Bulrush
	6.3	50	Mine Spoil/Cattail
	6.3	50	Natural Wetland/Cattail
	6.2	49	Acid Wetland/Cattail

13.9 mg/L (acid wetland/cattail) to 14.5 mg/L (natural wetland/cattail), tested significantly different (4 of 6 substrates) from influent values (14.8 mg/L) but absolute removal values were very low and statistical significance was inconsequential.

Seasonal comparisons of effluent values revealed that acid wetland/cattail significantly reduced dissolved Fe during winter (Jan-Feb) but other seasonal differences (Mar-Sept) in Fe or in other parameters were unclear.

Examination of the results for these parameters over time exposes a strong temporal pattern in removal efficiencies for all substrate/plant treatment types that was obscured by overall influent/effluent means (Figures 2-5). Declines in influent Fe and Mn concentrations, a concomittant increase in pH and extremely variable TSS values during the study period are unexplained, though possibly related to regional drought conditions.

Effluent values for TSS, dissolved Fe, and Mn suggested that low removal efficiencies during the first winter may have been due to (1) system initiation in late fall and (2) overloading during the first 10 weeks of operation. At an application rate of 0.5 L/min, efficiency improved but leveled off until warmer weather in early February. Removal efficiency gradually improved until mid April and rapidly thereafter. The pronounced pattern, common to all substrate types, suggested that microbial populations increased dramatically with warmer temperatures from mid February onward and renewed plant growth in April developed system capability to remove much of the Fe from the acid drainage influent. Results from the pea gravel cell showed similar but more variable declines in Fe content, Figure 2.

Since the effluent results are not statistically significant between substrates, the removal efficiency improvement pattern common to all experimental cells suggests a major biological component in the removal process. The plant-substrate-microbe complex that is important to water quality improvement will develop, without innocula, in the 6 substrates tested to date, indicating the ubiquitous nature of desirable microbial organisms in wetlands treatment systems (Gregory and Staley 1982).

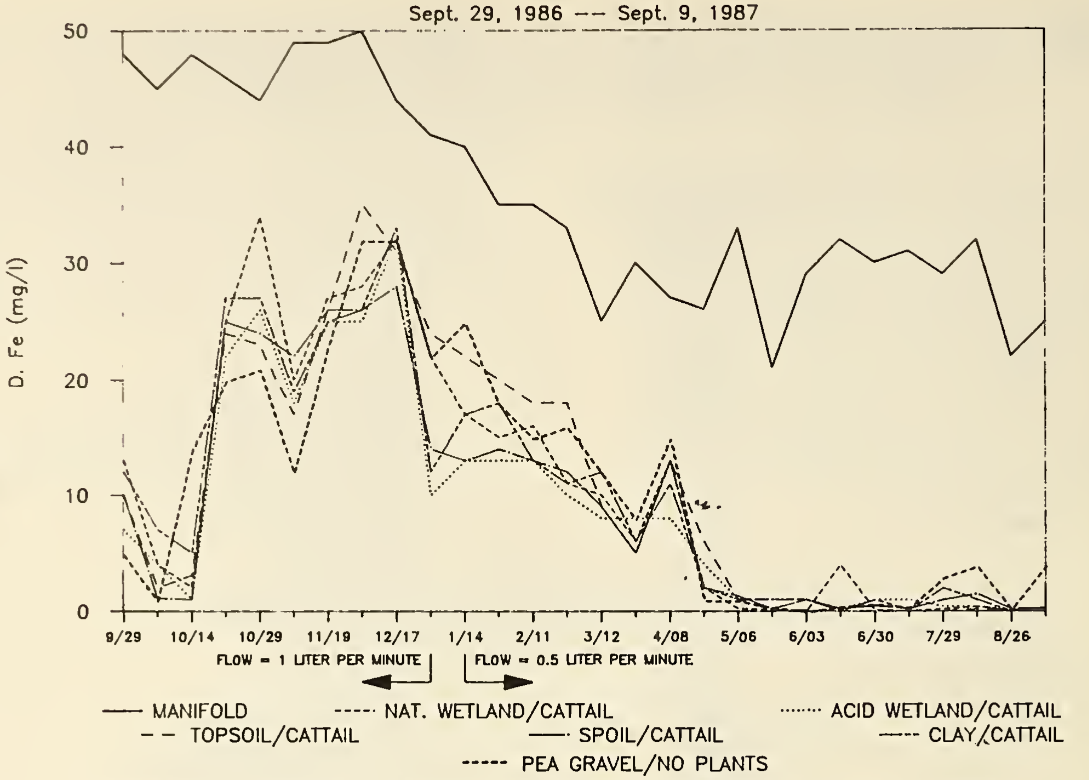

Figure 2. Effect of substrate type on dissolved iron in tests conducted at the Acid Drainage Wetlands Research Facility. Broken lines represent means of three replicated wetland cells, and solid line represents mean influent concentrations (manifold).

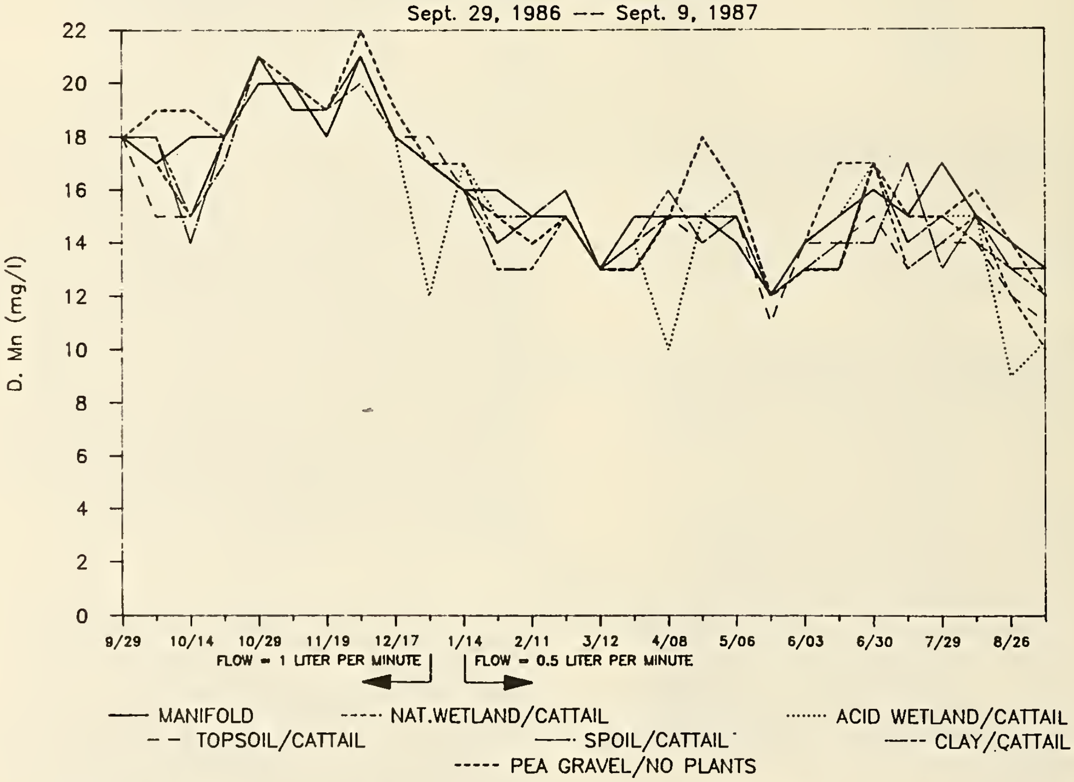

Figure 3. Effect of substrate type on dissolved manganese in tests conducted at the Acid Drainage Wetlands Research Facility. Broken lines represent means of three replicated wetland cells, and solid line represents mean influent concentration (manifold).

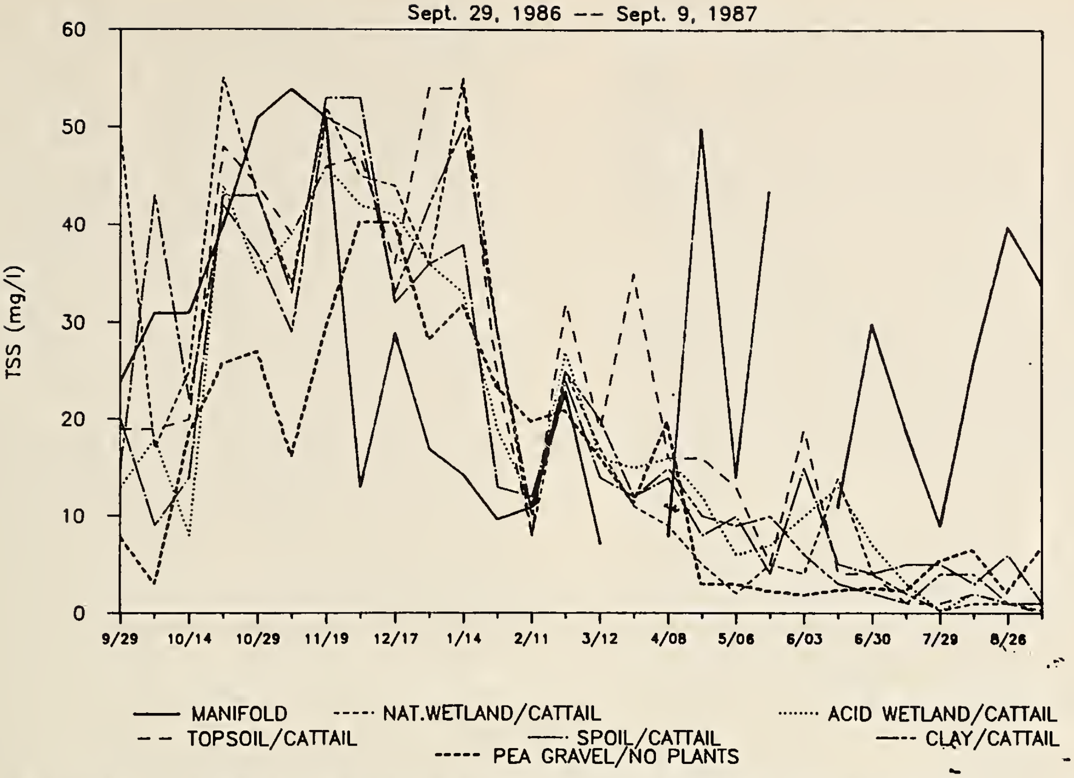

Figure 4. Effect of substrate type on total suspended solids in tests conducted at the Acid Drainage Wetlands Research Facility. Broken lines represent means of three replicated wetland cells, and solid line represents mean influent concentration (manifold).

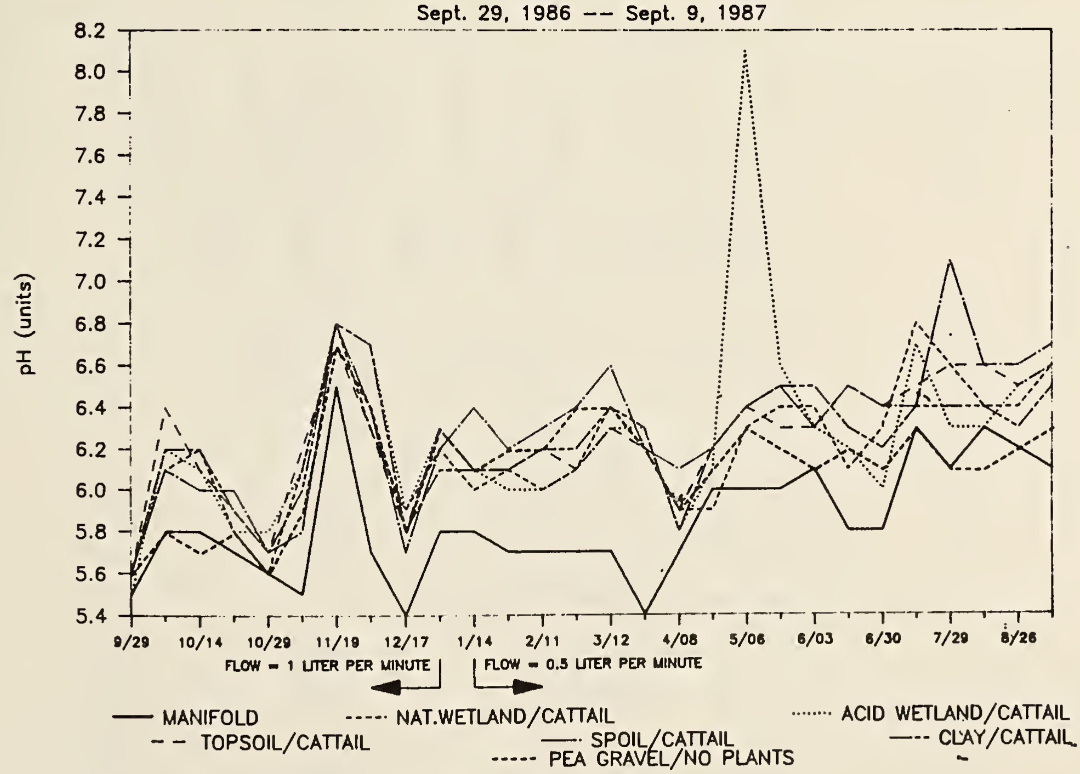

Figure 5. Effect of substrate type on pH in tests conducted at the Acid Drainage Wetlands Research Facility. Broken lines represent means of three replicated wetland cells, and solid line represents mean influent concentration (manifold).

Relatively poor removal of Mn, even at the end of the growing season compared to much greater removal in many operational systems (Brodie et al. 1988) suggested that the plant-soil-microbial complex does not substantially alter dissolved Mn compounds until after dissolved Fe is relatively low or unavailable for microbial metabolism. A lower influent application rate resulting in better dissolved Fe removal is likely to result in improved treatment of dissolved Mn.

Variations in influent and effluent pH seemed closely related although a similar gradual improvement over time was apparent. In contrast, a strong pattern of improved removal of TSS over time was evident despite widely varying influent values.

Though trends for pH and dissolved Mn are not readily apparent, substantial and consistent reductions in dissolved Fe and TSS even though influent values showed considerable variation, suggest that the plant-soil-microbial complex in wetlands treatment systems is amenable to considerable fluctuation in loading rates.

Interpretation of absolute effluent values in terms of wetland treatment system efficiencies must incorporate the application rates in use during these studies. A high application rate (0.5 L/min, ca 500 ft^2/gal/min, 0.4 m^2/mg Fe/min, Brodie et al. 1988) was deliberately selected to accentuate differences, if any, among different substrate types. Valve imprecision caused daily average flows to vary from 0.34 to 0.43 L/min compared to desired rates of 0.5 L/min. Acid and normal wetland substrates inadvertantly had higher flow (application) rates. Since these rates are substantially greater than recommended rates employed at 11 operating treatment systems (Brodie et al. 1988), these results must not be extrapolated to field scale operating systems.

In addition, cattail growing in all substrate types exhibited atypical root growth above the substrate and within the water column around each stem that was not present in operating wetland treatment systems. Visual inspection also revealed a consistent pattern of more vigorous stem and leaf growth in the upper portion of each cell as compared to the middle or lower portions.

Comparison of the average number of cattail stems from new shoots present at four times during the study revealed normal increases throughout the growing season but did not show significant differences between substrate types (Figure 6). Similarly, little differ-

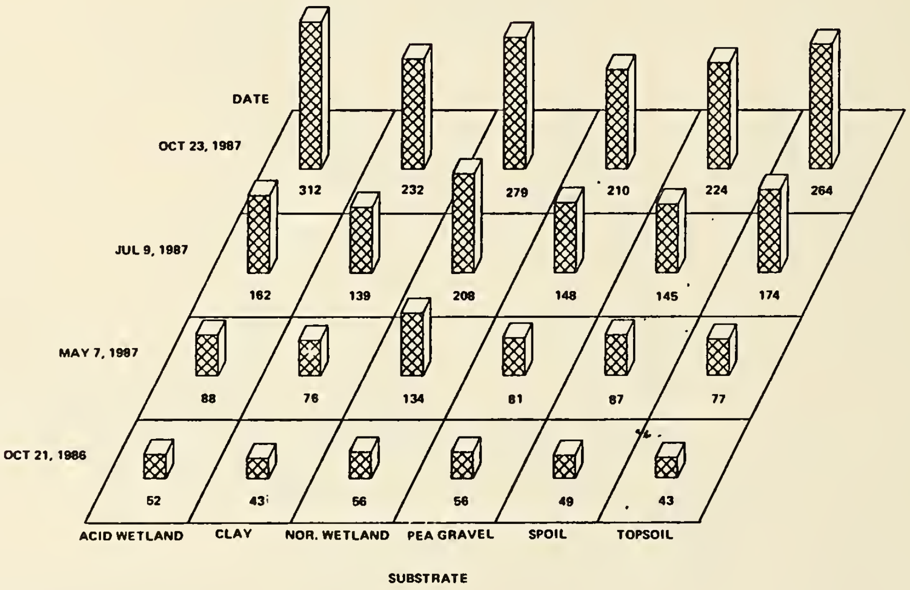

Figure 6. Mean number of cattail stems in experimental cells at the Acid Drainage Wetlands Research Facility, Jackson County, Alabama. One-way ANOVA's on each date showed no significant differences among replicated (3 cells) substrate types.

ence was apparent in height of cattail grown in different substrate types, though topsoil was a significantly better growth medium than pea gravel in July and significantly better than spoil and pea gravel in October. Analysis of phosphorus, total nitrogen and NH_3/ NO_3 nitrogen showed considerably more nitrogen content in the water in the upper portion of each cell and a similar difference in phosphorus and total nitrogen in cattail stems and leaves (Table 4).

Within-cell differences in cattail vigor appeared related to available nitrogen and phosphate in seep water and relatively low concentrations in substrate types. Excess fertilizer applied at initiation may have flushed out leaving influent seep water as the principal source for important plant nutrients resulting in atypical root growth in the water column. Since all cells exhibited atypical root growth and differences in cattail vigor were greater within each cell than between cells, these variables were unlikely to have differentially influenced the comparison of removal efficiencies in substrate types.

In summary, our results suggested (1) that substrate type is relatively unimportant to removal treatment efficiency since the desired plant-substrate-microbe complex became established in each type; (2) that microbial innocula were unnecessary; and (3) that vegetation may substantially improve treatment efficiency. From a practical standpoint, substantial

Table 4. Nutrients in water and sediment (October 10, 1987) and cattails (October 16, 1987) in three experimental wetland cells at the Acid Drainage Wetlands Research Facility, Jackson County, Alabama.

Wetland Cell	Location in Cell	Water (mg/L)	Sediment (mg/kg)	Cattail mg/kg dry wt)
		Total Phosphorus		
A5	upper	0.01	170	420
A5	middle	0.02	280	320
A5	lower	0.03	180	260
B6	upper	0.01	240	520
B6	middle	0.05	400	320
B6	lower	0.03	120	200
C5	upper	<0.01	350	960
C5	middle	0.01	240	400
C5	lower	0.02	170	320
		Total Kjeldahl Nitrogen		
A5	upper	0.20	330	4900
A5	middle	<0.02	310	3740
A5	lower	<0.02	310	2720
B6	upper	0.20	430	5810
B6	middle	<0.02	430	1980
B6	lower	<0.02	310	2780
C5	upper	0.16	340	7880
C5	middle	<0.02	360	3380
C5	lower	<0.02	250	4870
		Ammonia Nitrogen/Nitrate Nitrogen		
A5	upper	0.51/0.02	--	--
A5	middle	<0.01/0.01	--	--
A5	lower	<0.01/<0.01	--	--
B6	upper	0.51/0.02	--	--
B6	middle	0.01/0.02	--	--
B6	lower	0.01/0.01	--	--
C5	upper	0.50/0.03	--	--
C5	middle	<0.01/0.02	--	--
C5	lower	<0.01/0.01	--	--

differences must exist between substrate removal efficiencies to justify the considerable construction costs entailed in deliberately installing a specific substrate in field scale operating systems.

The functional values of wetlands vegetation previously identified from operating system results were supported by analysis of these data, i.e., substrates with emergent vegetation had higher removal efficiencies than substrates lacking vegetation. A better understanding of wetlands vegetation is anticipated from the results of future comparisons of removal efficiencies of different wetlands vegetation at the Acid Drainage Wetlands Research Facility.

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ISOLATION AND CULTURE OF A MANGANESE-OXIDIZING BACTERIUM FROM A MAN-MADE CATTAIL WETLAND

Vail, W. J. (1), Wilson, S. (2), and Riley, R. K. (3). ((1) Professor and Chairman, (2) Student, and (3) Professor, Department of Biology, Frostburg State University, Frostburg, MD). A manganese-oxidizing bacterium was isolated and cultured in association with a fungus from a cattail wetland. Sediment and water samples were collected from a man-made cattail wetland in Somerset County, PA during the summer of 1987. Winogradsky columns were prepared, and the columns were sampled and transferred to tubes containing a medium composed of manganese sulfate and yeast extract at pH 4. After 3 days incubation a fungus mycelium appeared, and after 3 additional days incubation the mycelium began to turn dark. Microscopic examination showed many regions associated with the hyphae containing dark brown crystalline deposits which are assumed to be manganese dioxide. The fungus grown on the control medium, which lacked manganese sulfate, produced a cream-colored mycelium, but did not exhibit these brown deposits. Using standard microbiological techniques, a fungus-bacterium association was isolated, and observed and confirmed with SEM. The oxidization of Mn occurred at pH 4 and above. When this association is inoculated into a medium of manganese sulfate and yeast extract, there is a reduction of [Mn] in the supernatant fluid of between 18 to 26 percent over a 12-day period. The bacterium was tentatively identified as *Metallogenium*, and attempts are underway to grow both the fungus and bacterium in separate cultures.

Additional Key Words: *Metallogenium*.

SCREENING OF MOSSES AND ALGAE IN GREENHOUSE EXPERIMENTS FOR THEIR ABILITY TO REMOVE IRON FROM WATER.

Webster, H. J. (1), Stark, L. R. (2), and Stevens, S. E., Jr. (3). ((1) Assistant Professor, Biology Department, Dubois Campus, The Pennsylvania State University, DuBois, PA 15801, (2) Research Associate, Biology Department, The Pennsylvania State University, University Park, PA 16801 and (3) Professor, Molecular and Cell Biology, The Pennsylvania State University, University Park, PA 16802). Greenhouse experiments were conducted to screen the potential of five moss species, one algal species, and sawdust for their effectiveness in lowering the concentration of iron in acidified water. The initial iron concentrations of the reservoir water were 37-45 mg/L, using $FeSO_4$ as the source of iron. The pH for each species was adjusted to the pH of the water at the collection sites as follows: *Sphagnum recurvum* (5.2), *S. fimbriatum* (5.5), *Drepanocladus fluitans* (5.2), *Pohlia nutans* (2.8), *Aulacomnium palustre* (5.5), and *Ulothrix subtilissima* (3.1), while the red oak (*Quercus borealis*) sawdust was screened at a pH of 5.5. Water flow rates were 60 mL/min through each system. The percent change in iron concentrations of the water varied with species, although direct comparisons among species should be made with caution. After 13 to 14 hours, the dissolved iron in outlet water had been lowered relative to inlet water as follows: *Spagnum recurvum* (92%), *S. fimbriatum* (78%), *Drepanocladus* (86%), *Pohlia* (50%), *Aulacomnium* (98%), *Ulothrix* (27%), and sawdust (49%). Iron-oxidizing microbes were associated with the plant species although no correlation was found between bacterial counts and the lowering of iron concentrations. The iron content of plant tissue was greatest near the inlet of each lane, and brown tissues had more iron than green tissues. These results suggest that certain mosses and algae may be effective in treating acid mine drainage.

Additional Key Words: wetlands, *Sphanum recurvum*, *S. fimbriatum*, *Drepanocladus fluitans*, *Pohlia nutans*, *Aulacomnium palustre*, *Ulothrix subtilissima*.

ECOLOGICAL ENGINEERING AND BIOLOGICAL POLISHING: ITS APPLICATION IN CLOSE-OUT OF ACID GENERATING WASTE MANAGEMENT AREAS

Kalin, M. (Ecologist, Boojum Research Limited, Toronto, Canada). Methods for establishing cattail stands on pyritic wastes are being developed as part of Ecological Engineering. Cattails reduce infiltration of precipitation and provide organic matter. Hand-transplanted, mature *Typha latifolia* L. developed into stands with significantly higher growth potentials when transplanted in groups comprised of >3 plants. Mechanical transplanting was more suitable in physically exposed locations, but was limited by machinery access. Although hydroponic transplanting failed in waters with high Zn and Cu concentrations (250 and 35 mg/L), growth was achieved in waters with 3 and 0.5 mg/L Zn and Cu. Effective metal removal by aquatic biota (biological polishing) from acidic waste water is a function of the annual biomass production and their adsorption/uptake characteristics. Biomass production of *Drepanocladus fluitans* (C. Muell.) Roth, transplanted in mesh bags into an acidified lake (pH 4.0) was seasonally dependent (maximum, 100 g [dry weight]/m^2 moss; July, August)., but not affected by location within the lake. Its polishing capacity ranges between 0.05 to 0.1, and 0.01 to 0.03 g/m^2 Zn and Cu. The biomass production of a gelatinous algal community, primarily *Muogeotia* Agardh spp., colonizing a substrate of submerged woody debris in the same lake, was dependent on location, but not on season. Biomass production in the first year of substrate introduction ranged from 9 to 42 g [dry weight]/100 g branch, while the polishing capacity of this periphytic algae-branch complex after 6 months of growth was 0.1 and 0.03 g /100 g branch Zn and Cu. Effective methods curtailing environmental degradation due to acid-generating base metal mining wastes can be developed through combining different polishing agents.

Additional Key Words: base metal mining, mine waste water, copper contamination, zinc contamination, *Typha latifolia*, *Drepanocladus fluitans*, *Muogeotia* spp.

WETLANDS AND MINE DRAINAGE - AN ECOTECHNOLOGY APPROACH

Mitsch, W. J. (1), Fennessy, M. S. (2), Cardamone M. A. (3), and Palmieri, D. (4). ((1) Professor, School of Natural Resources, The Ohio State University, Columbus, OH 43221, (2) Graduate Assistant, School of Natural Resources, The Ohio State University, Columbus, OH 43221, (3) Assistant Director, Wetlands Research Inc., 53 West Jackson, Chicago, IL 60604, and (4) Graduate Assistant, School of Natural Resources, The Ohio State University, Columbus, OH 43221. Ecotechnology and ecological engineering mean the purposeful matching and design of solar-powered ecosystems for benefit of both humans and nature. The control of acid mine drainage offers significant opportunities to explore the principles of ecotechnology. A general framework of the use of natural ecosystems for the "treatment" of water is presented, based on several years of wetland research in Kentucky and Ohio, followed by specifics of a case study in eastern Ohio. The case study involves a constructed, 0.25-ha wetland, organized into three cells of *Typha latifolia*, which is being used as an alternative control for acid mine drainage. Changing water quality and vegetation characteristics have provided a measure of the effectiveness of the wetland in removing dissolved iron from the mine effluent. Total reduction of iron from the mine water has averaged 57% within the system, with the largest proportion (21.3%) of the iron removal occurring in the third and final wetland cell, where vegetation density is greatest. The rate of iron removal is lower in the first two wetland cells, where vegetation density is also lower. Distribution of vegetation appears to be independent of distance from the mine effluent; it is controlled by the depth of standing water in the wetland. Growth (height and number of leaf blades) does not appear to be significantly affected by the mine water. If ecotechnology is to be successful in helping to control acid mine drainage, then design parameters and empirical models must be developed for the use of wetland ecosystems.

Additional Key Words: iron removal, *Typha latifolia*.

PEAT BLANKET TO LOCK ACID MINE SPOILS IN A SELF-SUSTAINING ECOSYSTEM

Brown, A. (1), Mathur, S. P. (2), and Kushner, D. J. (3). ((1) Graduate Student, Department of Biology, University of Ottawa, Ont., Canada, (2) Research Associate, Land Resources Research Centre, Agriculture Canada, Ottawa, and (3) Professor, Department of Biology, University of Ottawa, Ont., Canada). Acid leaching from pyritic mine tailings is due to microbial oxidation of iron sulphides which provides the energy source for the organisms. This conversion of sulphur to sulphate, and ferrous to ferric iron, is very inefficient and so requires a good supply of oxygen. Exclusion of oxygen from the tailings thus prevents acid leaching. It is proposed that covering mine spoils with a peat blanket will actively prevent access of oxygen, as waterlogged peatlands are a reducing environment where organic matter accumulates as aerobic microbial decomposition is inhibited. In this anaerobic environment, a consortium of microorganisms reduce the plant cellulose to methane and carbon dioxide. Initial experiments are reported here to establish in the range and distribution of methane in natural bogs and the conditions necessary for the cultivation of methanogenic bacteria. An array has been set up in Mer Bleue near Ottawa, where the methane was sampled from three depths over an area of 24 m^2. The amount of methane obtained from one station varied from 14 μmoles to 10 mmoles, with a total accumulation from all stations of over 130 mmoles. Laboratory incubations appear to show that the methane measured in the field occurs where it is produced. It is postulated that the pore spaces of the peat are plugged by insoluble methane which limits movement of oxygen, water, or methane itself to provide an impermeable cover.

Additional Key Words: methane, laboratory incubation, anaerobic environment, acid leaching.

WETLAND/RIPARIAN RECONSTRUCTION FOLLOWING SURFACE MINING: PART III. RECOMMENDATIONS ON CHANNEL MORPHOLOGY TO SUPPORT A WET MEADOW

Behling, R. E. (Professor, Department of Geology and Geography, West Virginia University, Morgantown, WV). Recommendations were formulated for reconstruction work on a 14-ha wetland/stream system, 927 m above sea level, which is being exposed through surface mining along Pendleton Creek, Tucker County, WV. This wet meadow is one of the numerous wetlands in the open-fold region of the Appalachian Plateaus in West Virginia and Maryland. The Pendleton Creek drainage basin is approximately 2.4 km wide, and the valley floor is 190 m wide. Fine-grained alluvium mantles the colluvium and bedrock to a depth of 2-3 m and forms the substrate for the natural wetland in the valley. The natural course of Pendleton Creek was a meandering channel, 4-5 m wide and 1.0-1.5 m deep. The gradient of the Pendleton Creek valley floor is less than 1 degree where the wet meadow exists. Sinuosity of the channel as determined from aerial photographs was 1.6. Bankfull width and depth measured in several locations between meander bends averaged 4.7 m and 1.4 m, respectively. Channel walls were nearly vertical with a curve at the base of the channel, creating a slightly concave floor. The natural channel is grass-lined. It is suggested that a grass-lined, meandering channel (sinuousity about 1.5), with rip-rap at the concave (outer) bank at meander bends would offer the greatest promise for all possible flow regimes of Pendleton Creek. The land adjacent to the channel could be returned to a wetland (a wet meadow would replicate natural conditions) and out-of-bank flow would be encouraged. A trapezoid cross-section for the channel of side slope 1.5:1; bottom width 3.0 m; depth 1.0 m would reflect bankfull conditions similar to those existent under natural conditions.

Additional Key Words: stream hydrology, reclamation, stream flow path, controlled flooding.

A STAGED WETLAND TREATMENT SYSTEM FOR MINE WATER WITH LOW pH AND HIGH METAL CONCENTRATIONS

Demko, T. M. (1) and Pesavento, B. G. (2). ((1) Geologist, P&N Coal Co. Inc., 240 West Mahoning St., Punxsutawney, PA. 15767 and (2) Consultant, Environment Analytic Service, Biological Filter Designers, Fredonia, PA). The use of man-made wetland ecosystems to renovate mine discharges has mainly been limited to low to moderate concentrations (10-100 mg/L) of iron, manganese, and aluminum. In order to study such a system under more adverse conditions, a wetland ecosystem complex has been designed and constructed to treat a mine discharge in western Elk County, PA, which is characterized by high concentrations of iron (100-400 mg/L), manganese (150-550 mg/L), aluminum (50-200 mg/L), and sulfate (8,000-12,000 mg/L), and a low pH (2.5-3.2). The flow rate varies seasonally and reacts quickly to precipitation and snow melt events, but averages 12 gal/min. The wetland ecosystem complex was designed to remove the high metal loadings by three mechanisms or groups of mechanisms: (1) the staged, biocatalyzed oxidation/precipitation of the metal ions and complexes in solution; (2) co-precipitation (adsorption, chelation, ion-exchange) of metal ions and complexes by iron, manganese, and aluminum oxides and hydroxides; and (3) inorganic geochemical precipitation. The wetland complex consists of six stages separated by flow and level control structures and aeration drop structures. The stages are, in downstream order: an algae and moss pool, four separate typha-algae cells, and finally, a polishing pond. Preliminary results from the first year of treatment have shown that the acidity of the discharge has been reduced by two-thirds (2,500 mg/L to 850 mg/L) and the iron concentration has been reduced by three-fourths (400 mg/L to 100 mg/L). The transplanted and volunteer wetland vegetation have flourished in the lower two-thirds of the wetland during the first growing season. Metal precipitates have accumulated to depths of 1.5 inches in the upper portion of the wetland. Flow has been reduced by one-fifth by evapotranspiration during the summer and early fall. Data from the second growing season are now being collected, and increased efficiency of treatment is expected.

Additional Key Words: acid mine drainage, ecosystems.

CONSTRUCTION OF A WETLAND DEMONSTRATION SITE FOR A METAL-MINE DRAINAGE

Wildeman, T. R. (1), Laudon, L. S. (2), and Howard, E. A. (3). ((1) and (2) Department of Chemistry and Geochemistry, Colorado School of Mines, and (3) Department of Environmental Sciences and Engineering Ecology, Colorado School of Mines). At the Big Five Tunnel in Idaho Springs, CO, an EPA Superfund Site, a model wetlands ecosystem has been built. The project is sponsored by the EPA Region VIII Superfund Program and Camp, Dresser, and McKee under a contract to the Colorado School of Mines. Three 200 ft^2 pilot plants have been constructed so the fate of all entering chemicals can be established. The objective of the project is to determine in one year whether wetlands can be used as a cost effective first step in the treatment of metal-mine drainages. So far the following conclusions have been made: 1) The design was simple and the construction was straightforward (since all materials used were readily and locally available). 2) An area of 200 ft^2 was adequate to maintain a complete ecosystem. 3) Selection of plants from local environments was possible, but transplanting was difficult. Large scale transplanting will require a significant investment in labor and equipment. 4) The mechanical portions of the system have operated well through a winter that was more severe than normal. 5) The chemical and bacteriological removal of pollutants has been occurring through the winter even though the vegetation was planted in September when it had already started to turn dormant.

Additional Key Words: Superfund Program, acid mine drainage.

RESPONSE OF THIOBACILLUS FERROOXIDANS TO ORGANIC COMPOUNDS: LEAKAGE OF CELLULAR MATERIAL AND INHIBITION OF GROWTH

Bhatnagar, M. (1) and Singh, G. (2). ((1) and (2) Centre of Studies in Mining Environment, Indian School of Mines, Dhanbad - 826004, India). Chemolithotrophic bacteria, particularly *Thiobacillus ferrooxidans*, accelerate the oxidation of iron sulphide minerals. Materials toxic to these bacteria can be used to inhibit bacterial activity and control acid mine drainage (AMD). Iron oxidation by *T. ferrooxidans*, and growth on Fe^{2+} iron were inhibited by a variety of organic compounds including sodium benzoate (SBZ), sodium lauryl sulphate (SLS), potassium sorbate (PSB), and some organic acids under laboratory conditions. Experiments were performed with cultures of AMD-bacteria to determine the threshold concentrations required for bacterial inhibition by candidate compounds. Results of this investigation indicated that SLS, SBZ, and PSB in the concentration range of 8 to 10 mg/L and organic acids in the concentration range of 10^{-3} *M* to 10^{-2} *M*, effectively inhibited bacterial growth with an associated decrease in iron oxidation of about 70 percent. It is inferred that organic compounds either react with extracellular iron or affect the functions associated with the bacterial cytoplasmic membrane.

Additional Key Words: acid mine drainage, sodium lauryl sulphate, sodium benzoate, potassium sorbate, lipopolysaccharide, peptidoglycan, cytoplasmic membrane.

IRON MONOSULFIDE AND PYRITE FORMATION IN SEDIMENTS OF LAKES THAT RECEIVE ACID MINE DRAINAGE

Wicks, C. M. (1), Herman, J. S. (2), Mills, A. L. (3), and Schubert, J. P. (4). ((1) Graduate Student, (2) Assistant Professor, and (3) Associate Professor, Dept. of Environmental Sciences, Univ. of Virginia, Charlottesville, VA, and (4) Hydrogeologist, Argonne Natl. Lab, Argonne, IL). Lake acidification from acid mine drainage (AMD) is an important environmental problem. Acid mine drainage can be ameliorated by the production of the minerals iron monosulfide (FeS) and pyrite (FeS_2) in impacted lake sediments. The authigenic formation of FeS_2 and FeS is hypothesized to occur when ferrous iron reacts with dissolved sulfide (H_2S, HS^-), which is produced by microbially mediated sulfate reduction. The result is that iron, sulfate, and acidity concentrations are decreased, while bicarbonate alkalinity is increased. If the reaction occurs in sediments that receive abundant sulfate ions and organic matter, then iron will be the limiting reactant. As the iron concentration increases, the dry weight percent of FeS or FeS_2 in the sediments should increase. The objective of this study was to determine if porewater iron concentration could be used as an indicator of FeS and FeS_2 formation in the sediments. Samples of lake water, porewater, and sediment were taken from 14 lakes that receive AMD throughout the Appalachian, Eastern Interior, and Western Interior Coal Basins. Concentration ranges observed in the porewater samples were 0.1 to 1,500 mg/L Fe^{2+}, 0.25 to 4.2 mg/L Fe^{3+}, 2.6 to 1,850 mg/L SO_4^{2-}, and pH of 6.05 to 8.0. Values of Eh calculated from the ferrous-ferric redox couple showed oxic conditions existing in the porewater. However, the sediments were dark in color and smelled of hydrogen sulfide, indicating anoxic conditions. The porewater composition, a reducing Eh, and field pH were used in the computer model PHREEQE to predict the saturation state of the porewater with respect to FeS_2 and FeS. Based on these results, in 9 of the 14 lakes pyrite is predicted to be the stable mineral phase. The remaining 5 lakes are significantly undersaturated with respect to pyrite. Authigenic pyrite is not expected to be found in those sediments. For each of these lakes, the reaction is limited by low concentrations of either iron or sulfur. Molar Fe/S ratios in FeS_2 and FeS are 1:2 and 1:1, respectively. All undersaturated waters exhibit extreme departures from these ratios.

Additional Key Words: porewater composition.

HYDROLOGY AND GEOCHEMISTRY OF SURFACE COAL MINE LAKES

Schubert, J. P. (Hydrogeologist, Argonne National Laboratory, Argonne, IL). Lakes are commonly created in surface-mined areas when mine pits or low depressional areas in spoil materials are not completely backfilled and eventually fill with water after mining operations have ceased. These lakes often contain good-quality water and have great potential post-mining benefits, such as swimming, boating, fishing, wildlife habitat, and even drinking water supplies. Some lakes, however, are very acidic (e.g., $pH < 4.0$) and contain deleterious concentrations of sulfate, iron, manganese, and other trace metals. A study was initiated in an attempt to determine the hydrologic and geochemical characteristics of mine sites that may be controlling water chemistry in the manmade lakes. Twenty-one lakes in the Eastern and Central U.S. have been intensively sampled. Five lakes had pH values between 2.5 and 5.0, three lakes had pH values between 6.0 and 7.0, eight lakes were between 7.0 and 7.5, and five lakes had pH values greater than 7.5. Hydrologic variables such as infiltration rates, hydraulic conductivity, and texture of spoil materials have been measured. Geochemical analyses of soil, spoil, and lakebed samples included: pH, electrical conductance, cation exchange capacity, exchangeable cations, total sulfur, and neutralization potential. Multivariate statistical procedures have been utilized to determine which watershed characteristics, hydrologic variables, geochemical parameters, or lake morphometric variables are the most influential on the resulting water chemistry of mine lakes.

Additional Key Words: acidity, trace metals, watershed characteristics.

WATER RESOURCE DEVELOPMENT ENGINEERING AND ACID MINE DRAINAGE IN THE UPPER OHIO RIVER BASIN

Koryak, M. (Limnologist, U.S. Army Corps of Engineers, Pittsburgh District). Acid mine drainage from bituminous coal mines has been the greatest single water pollution problem in the upper Ohio River Basin. Thousands of miles of streams within the western Pennsylvania, northern West Virginia, western Maryland, and southeastern Ohio portions of the basin have been degraded by an acid mine drainage (AMD) load that, until recent decades, was equivalent to more than a million tons/year of sulfuric acid. Severe AMD pollution caused damage by corroding pipes, pumps, boats, gates, and navigation aids. The acid and associated mineralization, and the frequent gross heavy metal pollution degraded the aesthetic and recreational value of local waters. The AMD suppressed and often totally eliminated aquatic life in local impoundments and along substantial reaches of major rivers, and it caused numerous and serious domestic and industrial water supply problems. Because of the extent and magnitude of the problem, AMD considerations have had a significant influence on many aspects of water resource development engineering in the upper Ohio River Drainage Basin. In some areas, AMD necessitated the use of special construction techniques and corrosion-resistant materials, and it increased and complicated maintenance problems. It was a major influence on the planning, design, and operation of large civil works engineering projects constructed prior to passage of the 1972 Clean Water Act. Reservoir operation schedules were developed as integral parts of Corps of Engineers reservoir projects to moderate low-flow AMD degradation extremes. As dramatic progress has been made recently in AMD abatement, these projects and operations continue to provide, for the most part, very substantial AMD mitigation benefits.

Additional Key Words: heavy metal pollution, water resource development, upper Ohio River Basin.

AERATION EFFICIENCY OF THE IN-LINE AERATION AND NEUTRALIZATION SYSTEM

Ackman, T. E. (1) and Hustwit, C. C. (2). ((1) Mining Engineer, U.S. Department of the Interior, Bureau of Mines, Pittsburgh Research Center and (2) Project Engineer, Boeing Services International). Acid mine drainage treatment typically involves the removal of soluble metals by neutralization, oxidation, and precipitation. The chemical reactions are frequently limited by the availability of dissolved oxygen. For this reason a study was conducted in the laboratory to establish the aeration efficiency of the In-Line Aeration and Neutralization System (ILS). This patented treatment system, developed by the Bureau of Mines, treats mine discharge in a pipeline and involves no moving parts. It consists of two components: a jet pump and a static mixer. Testing procedures were performed in accordance with the American Society of Civil Engineers (A Standard for the Measurement of Oxygen Transfer in Clean Water). The standard requires deoxygenation of a tank of clean water before aeration. The dissolved oxygen concentration in the water is measured over time as it is continuously pumped through the ILS until saturation is achieved. Corrections are made for ambient water temperature and barometric pressure. A total of twenty-eight tests were conducted using two different jet pumps and seven types of static mixers. Each combination of jet pump and static mixer was tested at two operating pressures: 20 psig and 50 psig. The results indicated that there were significant differences in aeration efficiency based principally on the water pressure. All systems transferred more oxygen when operated at 50 psig. Differences between the two jet pumps and four of the mixers do not appear to be significant. The Standard Oxygen Transfer Rates (SOTR) for the best jet pump/static mixer combinations are comparable to those cited by manufacturers of mechanical type aerators.

Additional Key Words: oxidation, aeration, sulfite, water treatment, acid mine drainage.

TREATMENT OF ACIDIC COAL REFUSE BY ADDITION OF CRUSHED-STONE POND SCREENINGS

Stokowski, S. J., Jr. (1) and Gilbert, R. R. (2). ((1) Consulting Geologist, Ashland, MA and (2) Civil Engineer, Adger, AL). Acidic refuse from Warrior Basin (AL) coal was treated with carbonate-rock, crushed-stone pond screenings, resulting in an improvement in the pH from 2.9 to 6.6. $Fe(OH)_3$ (yellowboy) formed on the treated waste and in ditches. Consequently, the pH of the runoff water improved from a range of 2.2-2.6 to a range of 4.4-6.2. Aqueous Ca and Mg concentrations and specific conductivity also increased. The water color changed from red to blue-green, possibly due to the iron oxidation state. The improvements have persisted for over 2 years from a single application of 54 tons/acre. The treatment process consisted of: 1) grading and ditching the refuse, 2) dumping the pond screenings and spreading with a bulldozer, 3) discing the material into the upper 6 inches of refuse, and 4) monitoring pH and other chemical variables in the refuse and surface-water runoff. After a few months of stable, near neutral pH conditions, grass was planted and is still vigorous. The refuse is waste material from the processing of coal, and is 6 inches and finer in size. It consists of shale that often contains marcasite, shale interbedded with coal and nodules or iron-pyrites with attached coal. The surface of the pile readily weathers into an impermeable, fine-grained layer. The pond screenings used are a byproduct of limestone/dolomite aggregate (Knox Group, AL) washed for concrete and other uses. They are especially finely graded (98% passing #50 sieve, 87% passing #200 sieve, 80% passing #325 sieve) because coarser fractions are removed by hydrocyclone for use in other products. The finest fractions are discharged to a sedimentation pond and recovered by dragline. Stockpiling and free drainage reduces the moisture content to acceptable levels. The fine gradation and chemical composition (79% $CaCO_3$, 14% $MgCO_3$) make the product an efficient neutralizer of coal mine acids.

Additional Key Words: reclamation, limestone, dolomite.

X-RAY DIFFRACTION EVALUATION OF COAL OVERBURDEN NEUTRALIZATION POTENTIAL

Despard, T. L. (Geologist, Office of Surface Mining Reclamation and Enforcement, Knoxville, TN). The Federal Regulations established to implement the Surface Mining Control and Reclamation Act of 1977 (SMCRA) require the identification of acid/toxic overburden strata and coal and the determination of the potential for such materials to adversely impact ground- and surface-water resources. The net acid-base account method is widely used to determine the acid/toxic potential of coal-bearing strata. This method is unreliable when applied to noncalcareous rocks because in these, the analytically determined neutralization potential is primarily due to silicate minerals, which react slowly with acid generated from pyrite oxidation. Leach testing has been used as an alternative to the net acid-base account method as a predictor of acid-mine drainage production; however, these tests are expensive and time-consuming. Determining the carbonate mineralogy of overburden strata, in conjunction with the net acid-base account, can greatly assist in predicting the effectiveness of the measured neutralization potential. X-ray diffraction (XRD) analysis can determine carbonate mineralogy both on a qualitative and semiquantitative basis, and the analyses can be accomplished rapidly. For the carbonates, calcite, dolomite, magnesite, and siderite, the required scan range is only from approximately 20° 2θ to 33° 2θ, and can be accomplished in minutes. Computer routines are available that can compute the percentage of calcite, dolomite, magnesite, and siderite in rock samples and can be expanded to include other mineral species if desired. These routines are derived from the generalized basic equation of X-ray quantitative analysis:

$$I_i = \sum_j c_{ij} x_j \quad i = 1,2, \ldots\ldots, m, \quad \text{where } c_{ij} = K_{ij}/\rho_j u\overset{*}{T}$$

Additional Key Words: overburden mineralogy, AMD prediction, acid-base accounting, carbonates.

STREAM SEALING OVER AN ACTIVE LONGWALL PANEL

Ackman, T. E. (1) and Hustwit, C. C. (2). ((1) Mining Engineer, U.S. Department of the Interior, Bureau of Mines, Pittsburgh Research Center and (2) Project Engineer, Boeing Services International). Stream infiltration losses associated with longwall mining activities can initiate environmental and mining hazards. In order to identify potential stream loss zones that might occur as a result of active longwall mining, the Bureau of Mines in cooperation with Southern Ohio Coal Company/Martinka Division instituted a study of surface water flow along a 1,400-ft section of Guyses Run, located near Fairmont, WV. Seven stream gaging and forty electromagnetic conductivity stations were established in July 1987, about 3 months before passage of a longwall panel beneath the stream section. Analysis of survey data collected within the stream channel permitted identification of a 300-ft zone of highest probability for stream infiltration losses. Conductivity surveys of the fracture system beneath the adjacent flood plain also confirmed the location of a potential infiltration loss zone in the stream channel. During the passage of the longwall panel beneath the predicted 300-ft loss zone, a complete stream loss event occurred within this section. Total water infiltration into the mine was estimated to be between 500 and 700 gal/min. Immediate steps to restore the streamflow involved sealing the channel with high-pressure injections of polyurethane grout. Approximately 11,800 lb of grout were injected through 153 grout rods located within the stream channel loss zone and along the contiguous channel banks. The rod emplacement depths varied between 3 and 6 ft. Within a few hours after completion of grouting, surface water flow was restored to the stream. This streamflow restoration virtually eliminated water infiltration into the mine. Post-grouting conductivity and stream gaging measurements have shown a flow pattern consistent with premining activities, and water infiltration into the mine has continued to be minimal.

Additional Key Words: electromagnetic conductivity, stream infiltration, stream losses, polyurethane grout.

MICROMAP -- A DATABASE RETRIEVAL AND DISPLAY MANAGER FOR MICROCOMPUTERS

Rymer, T. E. II (1), Renton, J. J. (2), and Stiller, A. H. (3). ((1) Research Associate, Departments of Chemical Engineering and Geology, West Virginia University, (2) Professor, Geology Department, West Virginia University, and Geochemist and Head of Analytical Section, West Virginia Geological and Economic Survey, and (3) Associate Professor, Chemical Engineering Department, West Virginia University). A new software package has been developed called "MICROMAP" to expand the capabilities of the Coal Reclamation Information System (CRIS) computer software developed in an earlier project funded by the West Virginia Dept. of Energy through the West Virginia Geological Survey. The CRIS software allowed the user to extract information from a database containing general mine information, water quality data, overburden analyses, and reclamation-revegetation data for surface mines in 12 northern West Virginia counties using a variety of geographical related retrieval modes (county-wide, 7.5 minute quadrangle, radius of a desired coordinate, and watershed). Unlike the original mainframe software, MICROMAP is able to run on any IBM/PC compatible microcomputer. The computer displays a map of any county(ies) requested by the user. The locations of surface mines that are in file, overburden drill core locations, and water sampling locations are pinpointed on the map. Data are extracted by moving a small graphics cursor to any location on the map and designating a square mile search area. The computer will then retrieve the general mine information, water quality data, and overburden analysis data for the designated area and move it to a display manager where it can be viewed on the screen and, if desired, channelled to a hard copy printer. In addition, a 7.5 minute quadrangle search mode is available, where the user need only specify a desired quadrangle. The original CRIS data sets have been subsetted into smaller, county data sets. The original master data set still resides on the mainframe where it can be updated and revised. The mainframe computer system generates the smaller county-wide data sets and moves these data sets to floppy disks. There are neither statistical nor graphical options available with MICROMAP as it is primarily a data search and retrieval display manager. Its chief advantage is its mobility and ready, easy access requiring only a microcomputer. The map graphics are highly accurate. It is possible to display Preston County, WV and Fayette County, KY on the same screen and still retain very good resolution and search capabilities. The mapping algorithm used is an efficient modification of the gnomonic method of map projections. MICROMAP has the capabilities of displaying all 55 West Virginia counties and corresponding datasets with minimized distortion on a medium resolution IBM color graphics screen.

Additional Key Words: mine sites, water quality, water sampling, CRIS, West Virginia.

INSTALLATION AND STABILITY OF INVERTED PYRAMID-SHAPED PLUGS FOR CLOSING ABANDONED MINE SHAFTS GALENA, KS DEMONSTRATION PROJECT[1]

John S. Volosin[2]

Abstract.-- The Bureau of Mines designed and installed 11 inverted- pyramidal- shaped plugs in a mine closure demonstration project completed in Galena, KS in December 1983. The demonstration project resulted from a study done by the Geological Surveys of Missouri, Kansas, and Oklahoma for the U.S. Bureau of Mines in January 1983. This study identified over 1400 open mine shafts and nearly 500 subsidence collapse features that remained from the original 14,000 shafts sunk in the Tri-State Zinc-Lead Mining District. In Galena, KS, alone over 377 open mine shafts were readily accessible and 150 abandoned mine shafts were within the city limits. Of these, the Bureau of Mines selected 14 abandoned sites for the mine shaft closure demonstration project. During the demonstration project, 11 mine shafts were closed with the inverted pyramid shaped reinforced- concrete plugs, 2 were closed with reinforced concrete caps after backfilling, and one shaft was closed by backfilling only. The stability of the closure devices has been monitored and evaluated over a 3-year period. The results indicate that the Bureau of Mines closure devices are stable and have eliminated hazards associated with open mine shafts in a populated area.

Introduction

The Bureau of Mines operated a shaft closure demonstration project in Galena, KS, in which 14 abandoned mine shafts were closed. The primary purpose of the project, which was part of the Bureau's program for conserving land resources, was to provide alternative methods for closing some of the hundreds of open shafts in the Tri-State area. The project developed from a study to evaluate the hazards of the abandoned zinc-lead district.

The Galena field is in the Tri-State zinc-lead belt district of Kansas- Missouri- Oklahoma, which was one of the largest zinc-lead mining districts in the country. The district produced over 11 million tons of zinc and 2.8 million tons of lead during its 122 years of operation. The total value of the lead and zinc produced in the district from 1850 through 1970, in terms of recoverable metal, was $2,073,200,000. In terms of today's dollars, the value would be in the neighborhood of 20 billion dollars (Stewart 1986, Martin 1946)

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the American Society for Surface Mining and Reclamation and the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, P.A.

[2] Metallurgist, Rolla Research Center, Bureau of Mines, Rolla, MO.

Mining began in the Tri-State district in 1848 with the discovery of ore deposits in Joplin, Mo. The deposits were originally mined for their lead value, but the development of the railroad in the area and the coincidental development of the new milling and smelting techniques for zinc resulted in the area becoming a valuable source of zinc. Zinc production in the district began with the first shipment of concentrates to LaSalle, IL in 1872. Later shipments went to the smelter in Weir City, KS constructed in 1873. By 1875, the Joplin field became the leading zinc producer in the USA. Additional lead-zinc deposits discovered west of Joplin increased mining activity. The Galena, KS, field was discovered in 1877. In 1891, lead mining began in Indian Territory (northeast Oklahoma), near Peoria, and ore discoveries followed near Lincolnville, Miami and Picher. The Commerce, OK, field was discovered in 1905. Large scale mining started in the Miami-Picher, OK, field in 1916. Mining continued in the Missouri portion of the district until 1957 and in the Kansas-Oklahoma portion until 1970.(Dressel et.al. 1986, Fejes et.al 1985, U.S. EPA 1975)

Early mining leases were generally small with many leases being only 100 or 200 ft^2 (Clerc 1907, Hay 1893, Hayworth 1901, Norris 1968, Plyn 1904). The ore was mined by small crews of men using hand tools and simple hoisting devices. Exploration was done by sinking a shaft, generally 50 to 100 ft deep, until ore was found. Exploration continued by drift mining outward from the shaft (Crane 1901). If ore was not encountered, the miner moved to new ground and sank another shaft. The mines were generally developed with little regard to any long-range overall mine plan. If drifts reached 300-ft in length or if ventilation became difficult, additional shafts were sunk. In most cases, the underground mine workings were not mapped.

In Galena, KS, the mining depths varied from ground surface to 300 feet. The ore was generally confined to thin bedded strata, and ore bodies were usually less than 30 feet thick. But, in some cases, ore zones 80 to 100 feet in thickness were developed. The ore was worked from the upper portion of the ore down to the depth at which water became too much of a problem to continue mining. When pumping facilities were installed, some of these mines were reopened and mining of the thick ore deposits resulted in rooms as much as 100 feet in height. In 1893, Henrich reported that diamond drills were being used for prospecting deeper than 100-ft. By about 1900, the churn drill replaced shaft sinking as the principal exploration tool (Gibson 1972, Plyn 1904).

The use of shafts as a means of exploration and the small lease and subleasing of mining plots resulted in a high density of mining shafts in the area. In preparing a series of reports for the Bureau, the State Geological Surveys of Kansas, Missouri, and Oklahoma located over 1,400 abandoned open mine shafts remaining of the original 14,000+ prospect and mining shafts sunk in the Tri-State district (Luza 1983, McCauley et.al. 1983, McFarland and Brown 1983). Although 90% of the original number of shafts have been closed, the shafts that remain open are constant safety and environmental hazards and limit the use of the land. In the Galena, KS, field alone, 377 open shafts were located within or adjacent to the city limits of Galena. All but 11 of these shafts showed surface enlargement because of cribing removal or failure.

Several methods have been used for closing shafts (Genie Eng. LTD 1983, NCB 1982). In the Tri-State shafts have been closed by backfilling and capped with timber caps, steel plates, concrete slabs, and railroad rail- gratings. However, in some cases the closure device failed and the shaft reopened to again become a safety hazard.

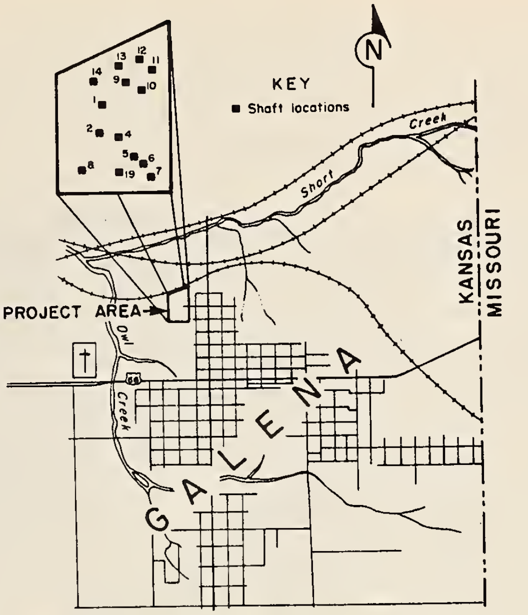
Backfilling was a common method for filling shallow shafts and it is still quite a successful method if done properly with graded material free of degradable trash and in a manner that avoids temporary bridging. Timber caps, rails, and steel plates have been used with varying degrees of success but eventually decay or rust, resulting in an unsafe closure. Although concrete caps have been successful in some instances, there are examples of failed concrete caps in the Galena, KS, area where the caps were improperly reinforced or where washout caused the cap to tip on end. In the Picher, OK, field, at least one company successfully used concrete cubes to close shafts when abandoning the field. The cubes, which were 6-1/2 ft on a side, were constructed on the surface next to the shaft and then rolled into the opening and wedged into place by undercutting and blasting.

Three methods were used for closing abandoned mine shafts during the Bureau's demonstration project described in this report. The newest method, the installation of the inverted pyramid-shaped plug designed by Bureau personnel, is discussed in detail. The results of 3- years of monitoring are also included. Additional details are available (Dressel and Volosin 1985).

SELECTION OF SHAFT SITES

Galena, KS, was picked as a site for demonstrating methods for closing abandoned shafts because of the large number of open shafts that were readily accessible. Before a location was selected for the demonstration, the Bureau contacted the Galena city government to ascertain which areas within the city limits were in the most need of shaft plugging. From the locations the city officials listed, the Bureau selected a site in NE1/4SW1/4 sec. 14, T. 34 S., R. 25 E., at the west end of Front, First, and Second Streets. Virtually all of the open mine shafts in Galena are on privately owned land. A search of the county land records was made to determine the ownership of the lands and the owners were contacted to obtain grants of easement that would permit the Bureau to carry on the demonstration project. Figure 1 shows location of the site and the location of the shafts closed during the demonstration. The breaks in the shaft numbering sequence resulted from changes in the original closure plan, brought about in one case because considerable construction debris had been dumped into the opening, and other cases because the locations were out of the area covered under the grants of easement.

Two of the open shafts selected for plugging are shown in figures 2 and 3. A contract was let in 1982 to obtain the shaft dimensions, assess the conditions of shaft side walls, obtain the elevation of an estimated contact between overburden and solid rock, and the location of underground workings in the shaft vicinity. These measurement were used in preparing the competitive bid specifications for the plug installations reported herein. Another contract was awarded in August 1983, to perform the actual closure demonstration work in which 11 shafts were plugged, 2 were cappped, and 1 was backfilled.


N
KEY
■ Shaft locations
14
13
12
11
9
10
1
2
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Short Creek
KANSAS
MISSOURI
PROJECT AREA
Owl Creek
66
GALENA

Figure 1.--Project site location.

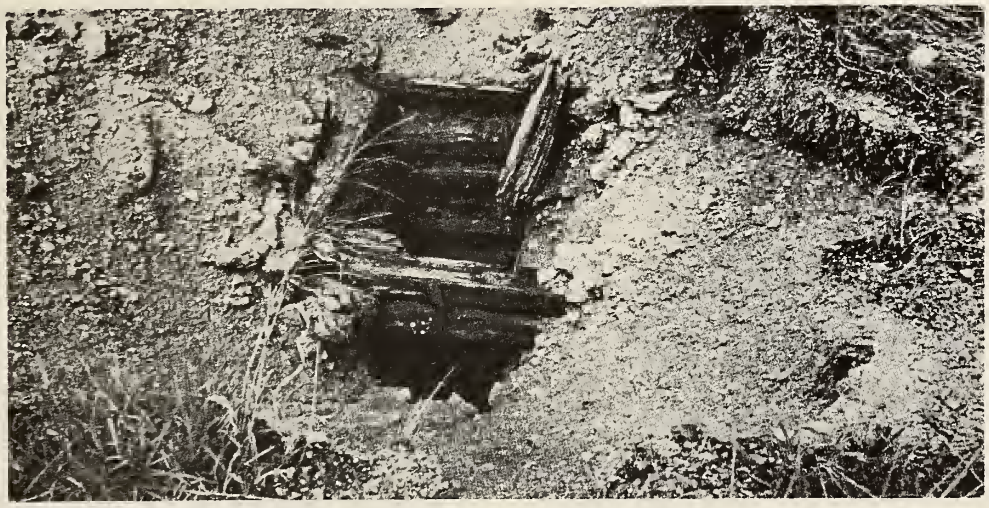

Figure 2.--Typical shaft showing rotted timber and washout along timbers.

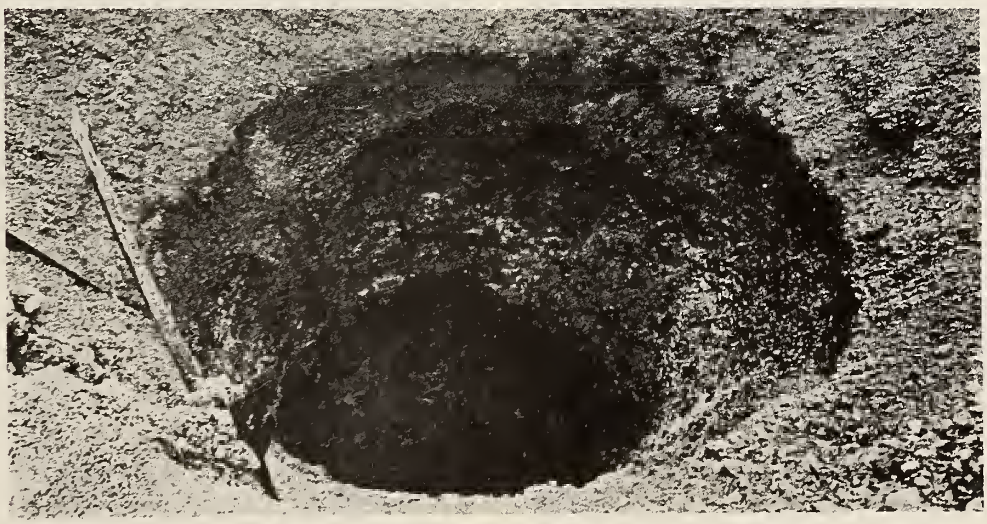

Figure 3.--Typical open shaft showing circular outline in slumping residuum.

DESIGN OF PLUG

An inverted pyramidal design was selected because it fulfilled the following criteria: (1) simplicity of construction, (2) ease of installation, (3) personnel safety during installation, and (4) permanency of the installed closure device. The shafts in this demonstration were roughly square and ranged in size from 4 to 8 ft. The pyramidal plug design was chosen because it was easily adapted to a variety of irregular mine shaft openings with a minimum amount of site preparation. When installed in a shaft, the center of gravity of the inverted pyramid plug could be placed so that the plug would have a tendency to adjust and wedge tighter into the shaft. A lightweight, prefabricated disposable form was designed that required a minimum amount of time to prepare and set in place without having to use heavy construction equipment. The form, complete with concrete reinforcement rods, was constructed in a welding shop away from the demonstration site and installed with a 17-ton crane.

The forms were designed to be totally self-supporting. Once they were set in place they were not anchored to any other structure within the mine shaft. They were constructed in three standard sizes of 8, 10, and 12 ft. The size for a given shaft was selected so that the top of the plug was approximately 4 ft larger on a side than the size of the shaft opening. The reference monument, a 4-inch pipe, long enough to extend above the surface level of the ground after backfilling, was attached to the center of the plug. A sketch of an installed plug is shown in figure 4.

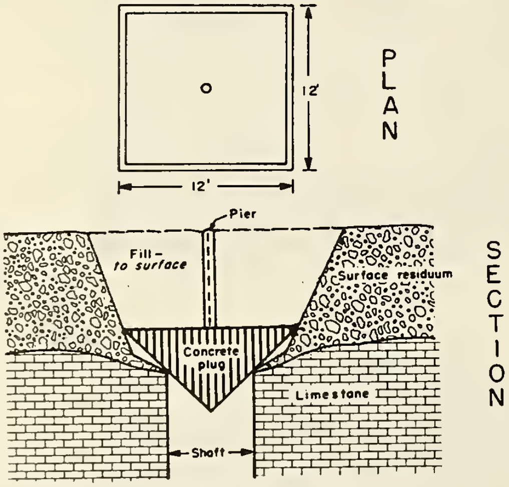

Figure 4.--Installed plug.

Eleven forms were required for the demonstration: 3 were 8-ft by 8-ft, 6 were 10-ft by 10-ft, and 2 were 12-ft by 12-ft. The 8-ft by 8-ft and the 10-ft by 10-ft forms were constructed of 3/16-inch hot-rolled low-carbon steelplate welded at the seams. The 12-ft by 12-ft forms were constructed of 1/4-inch hot rolled low-carbon steel. The external edges of the seams were reinforced by the addition of a fabricated angle, approximately 3-inches on an edge, welded to the seam. This reinforced edge proved very beneficial since much of the weight of the plug rested on the corners before seating. A plate was welded in each corner with an eyelet for attaching cables for easy handling and positioning the forms (fig. 5).

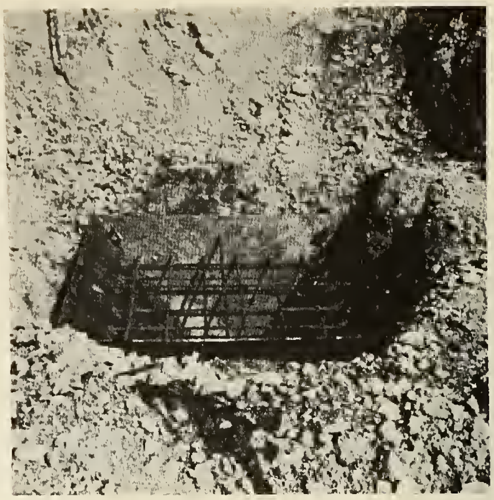

Figure 5.--Eight-ft form showing reinforcing grid.

A horizontal reinforcing rod grid was placed 1-ft from the top in the 8-ft pyramid forms, 1.25-ft from the top in the 10-ft forms, and 1.5-ft from the top in the 12-ft forms. A 12-inch grid spacing was used as shown in figure 5. Grade 60, No. 7 reinforcing bars were used in each instance.

In the 10-ft form, two S4 I-beams with 0.326-inch web thickness approximately 6 ft long, were welded to a 1/4-inch footplate which was welded to the sides of the form. The beams were arranged parallel to each other and spaced approximately equidistant from the parallel side walls and from each other (fig 6).

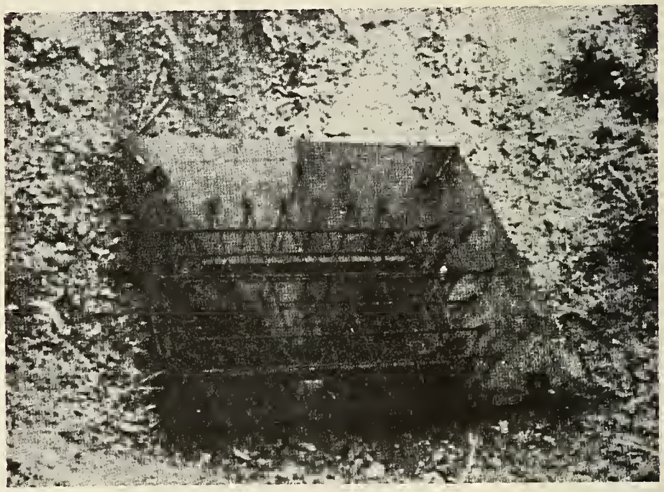

Figure 6.--Ten-ft form showing I-beam position and reinforcing grid.

To brace the side walls of the 12-ft form, two S4 I-beams, approximately 8 ft long with a 0.326-inch web thickness, were welded to the form at right angles to each other. The ends of these beams were welded to a 1/2-inch plate at least 1 ft^2, which in turn was welded to a second 1/2-inch plate at least 1 ft^2, previously welded to the inside of the form approximately 2-ft from the top (fig. 7).

Vertical reinforcing bars were placed 6 inches from each of the sloping sides of the pyramidal form (fig. 7). They were spaced 1-ft apart at the top of the form and tapered down to a few inches near the bottom. The top end of the rebars extended to within 6 inches of the top of the form. A spacer was welded approximately 1-ft from the top of each form to hold the rods 6 inches from the side walls.

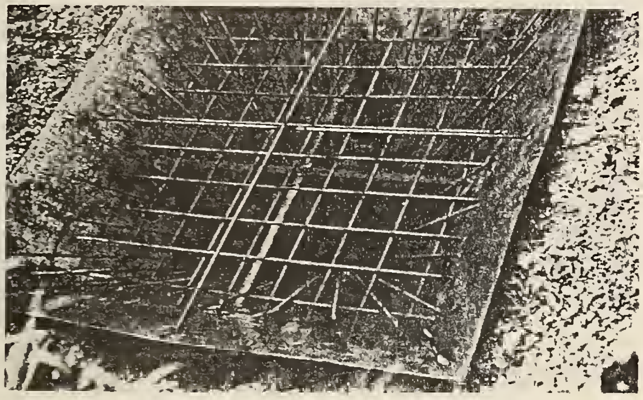

Figure 7.--Twelve-ft form showing I-beams and position of reinforcing bars.

Material requirements per plug are tabulated in table 1.

Table 1.--Material requirements per plug.

	Approximate shaft size		
	4-ft	6-ft	8-ft
Pyramid form size ...ft..	8x8x4	10x10x5	12x12x6
Metal preform........ft^2.	[1]90.51	[1]141.2	[2]203.6
Weight of metal form..lb.	693	1,083	2,079
Estimated rebars per shaft:			
Linear ft............	327	495	698
Weight...........lb..	660	1,020	1,420
I-beam:			
Length...........ft..	0	12	16
Weight...........lb..	0	89	118
Edge angle:			
Length...........ft..	27.7	34.6	41.6
Weight...........lb..	260	325	391
Total weight of steel.lb.	1,613	2,517	4,008
Concrete............yd^3.	3.2	6.2	10.7

[1] 3/16-inch cold-rolled, low-carbon steel plate.
[2] 1/4- inch cold-rolled, low-carbon steel plate.

INSTALLATION OF PYRAMIDAL- SHAPED PLUGS

A minimum of site preparation was required to prepare the shafts for plugging. The contractor used an Extenda-Hoe backhoe to remove sufficient material from around the surface of each open shaft to provide a roughly level contact of the disposable form with the interface between the surface residuum and the bedrock. The edges of the shaft at the interface were trimmed to allow the center of gravity of the form to be set below the interface elevation and to have a suitable bearing surface for setting the forms. Trimming was done with a jackhammer attached to the backhoe.

The pre-fabricated forms were delivered to the site on a flatbed trailer and were unloaded from the truck and placed directly in the hole using a 17-ton crane (fig. 8). In several cases, additional sidewall trimming using the backhoe and/or jackhammer was required to obtain a level postion for the forms.

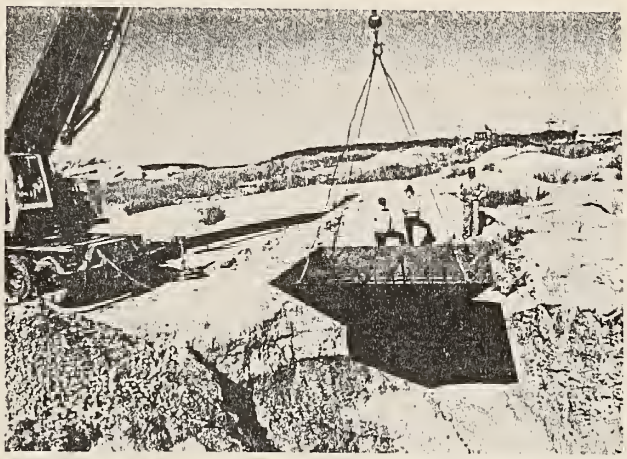

Figure 8.--Lowering 10-ft form into opening.

Class A concrete was delivered to the site from a local batch plant. Just prior to pouring, a reference monument was attached to the center of each plug (fig. 9). The 8-ft forms each required 3.2 yd^3 of concrete, the 10-ft forms 6.2 yd^3, and the 12-ft forms 10.7 yd^3.

After the first three plugs were placed, it was noted that there were gaps between the form and the sidewalls along the edge of the pyramid shaped form. In these areas, reinforcing bars were positioned over the edge of the form and extended to the side of the prepared opening. This was covered with a 2-ft width of expanded metal, and 4 inches of concrete was poured on this expanded metal.

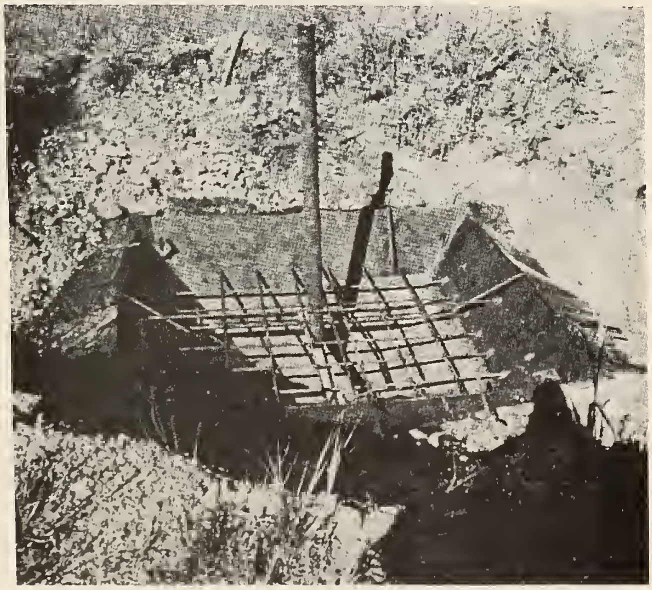

Figure 9.--Ten-ft form showing spider-leg reinforcing over edge of form to support the expanded metal.

Before pouring concrete in the last eight forms, steel reinforcing rod was bent and fastened to the installed horizontal reinforcing grid and extended in spider-leg fashion several feet over the edge of the form (fig. 9). The 2-ft wide expanded metal was positioned over these reinforcing rods, and concrete was poured over this when the form was filled (fig. 10). An additional 1 to 1-1/2 yd^3 of concrete was required for each shaft because of these modifications.

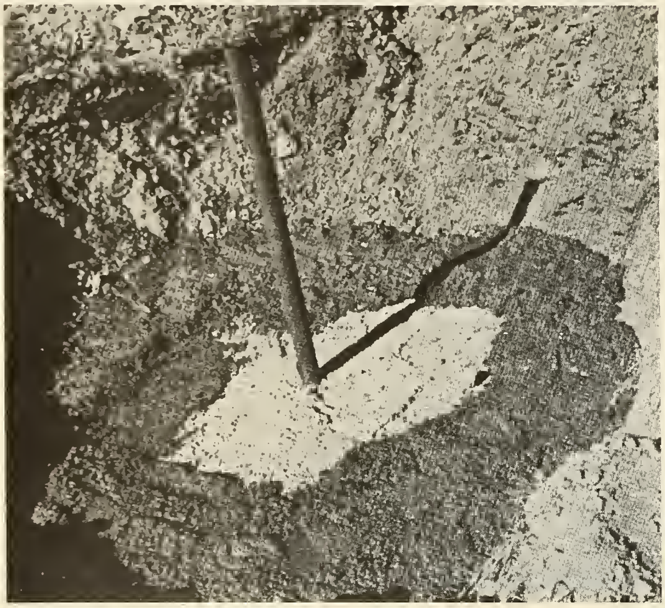

Figure 10.--Ten-ft form filled with concrete.

In the installation of one 12-ft and one 10-ft plug, the center reinforcing bars were left unwelded to the sides of the form to allow the form to bulge along the edges to better fill the gaps. This appeared to be an effective measure.

After a concrete curing period of at least 7 days, the excavated areas were backfilled with waste rock available near the shafts. The backfill at each site was mounded so that the center of the fill was approximately 2 ft above the surrounding ground surface. The 4-inch pipe extending from the center of each plug was trimmed so that it extended 6 inches above the fill; it was filled with concrete and was designed to remain as a marker for evaluation purposes.

INSTALLATION OF SLAB CAPS

In some instances, solid rock exposed at the surface was competent enough so that there was virtually no cratering or shaft enlargement at the surface. In these cases, it was found expedient to trim away loose surface rock and install reinforced concrete slabs. Two mine openings, approximately 4.5-ft by 4.5-ft, were closed by this method during the completion of the project.

The slabs were designed to extend approximately 5-ft over each edge of the open mine shafts. A reinforcing grid of No. 7 rebars was installed. The bars were spaced 1-ft apart at the edges, 1/2 ft apart in the area over the shaft opening, and located 1/2 ft from the bottom of the pad. A monument pipe was attached to the center of each grid, and an 18 inch thick pad of class A concrete was poured. The material requirements for each poured slab are shown in table 2.

Table 2.--Material requirements per slab.

Size of shaft............ft..	4.5x4.5
Dimension of slab.........ft..	15x15x1.5
Number of No. 7 rebars........	46
Total length of rebars....ft..	690
Total weight of rebars....lb..	1,420
Thickness of concrete.....ft..	1.5
Volume of concrete.......yd^3..	12.5

These slabs are of sufficient size and sufficiently reinforced to remain indefinitely without breaking or flipping over in the event of washout under part of the cap. They were also designed to withstand loads from automobile or truck traffic which may occur in the area following closure of the shafts.

INSTALLATION OF BACKFILL

In preparing shaft No. 14 for plug installation, the hole was found to be larger than original surface measurement had indicated, and it was difficult to obtain a stable bedrock surface. It became apparent that the alternatives were to either install a 16 ft plug, a 22 ft cap, or completely backfill the hole. Backfilling was chosen. This method, currently the locally accepted way to close a shaft, proved useful to this project in that it provided a reference for evalulating the closing of shafts by either plugging or capping abandoned mine shafts. Approximately 350 yd^3 of backfill were required to close the opening. A 4-inch pipe was placed at the shaft center as a marker for this closure.

DISCUSSION OF CLOSING DEMONSTRATION

A minimum of installation problems were involved and only a few changes were necessary in completing the planned demonstration program. The most serious problem was that no suitable underground maps were available for the demonstration site.

Working around abandoned mines shafts, particularly in areas where the extent of the abandoned underground mine working and the stability of the surface material around the shafts is not known, is potentially hazardous. Most of the abandoned mines are filled or partially filled with water. Water, encountered in all shafts during the mine shaft inspection performed by the contractor, made it difficult to determine if either the actual bottom of the shaft or a temporary bridge had been reached. Some shafts were filled with debris, such as old autos, air conditioners, and/or refrigerators. There was no way to get around or through debris at the bottom of the shafts. No debris was removed during the closure demonstration.

It also became obvious that the shaft dimension measurements made from the surface in these old hand-dug shafts before they were prepared for plugging were not entirely reliable. In several instances, measurements, made after the holes were prepared, required changes in plug size from original specifications. For example, the plug put in open shaft No. 19 was the plug originally constructed for shaft No. 14.

Sufficient waste rock was available on the nearby surface to backfill the openings over the installed plugs; most of the material trimmed from the shaft openings was allowed to fall into the open shafts. In one instance, temporary bridging of a shaft occurred during the trimming operation. This was to be expected because the material was ungraded, but it pointed out the necessity for using graded material when closing small shafts by backfilling.

The project was completed using a minimum amount equipment at the project site. Required equipment was a backhoe, a flatbed truck, a crane, and a concrete delivery truck. Care was taken to strategically locate the equipment around the shaft collar to avoid parking the vehicles above the underground mine workings and no more than two vehicles were at the shaft at anytime. The contractor and suppliers were informed of the possible hazards and proceeded with due caution and regard for personal safety.

The reinforcing rods were welded into position at crosspoints, and the ends were welded to the sides of the forms. This made the forms very rigid. The welding of the reinforcing rod ends at the center of the sides was omitted in several of the forms installed near the end of the demonstration. This enabled the form to bow out when filled with concrete to more nearly take the shape of the opening. However, when this happens, there are no reinforcing bars in the bowed part of the plug. A modified design that allowed the center reinforcing bars to extend through the plug walls might eliminate this problem.

Four plug forms were set in their respective shafts prior to a 7-inch rainfall. As a result, the forms were filled with water and had to be pumped out before the concrete was poured. Small drain holes were left in the last three plugs installed; however, the plugs were filled with concrete before the next rain.

EVALUATION OF CLOSURE DEVICES

After the 14 shafts were closed, the area around each closure device was backfilled to the rough surface elevation of the immediate area. Once this rough grade was established for the demonstration site, a 2-ft mound of fill was formed directly over each shaft and the tops of the reference markers for each shaft were trimmed to approximately 6-inches above the fill material. A local registered land surveyor was hired to establish a horizontal and vertical survey control net within the mine closure demonstration area. The initial elevation of the reference markers and the results of resurveys each year for a 3 year period are shown in Table 3.

Table 3.--Elevation of reference point on each closure device.

CLOSURE DEVICE	Survey results showing reference point elevation, ft			
In Shaft Number	12/23/83	10/31/84	9/27/85	11/14/86
8 FT PYRAMID PLUGS				
2	900.59	900.59	900.59	900.59
4	898.46	898.44	898.44	898.44
9	901.98	901.97	901.97	901.97
10 FT PYRAMID PLUGS				
5	890.74	890.74	890.73	890.72
7	897.49	897.47	897.47	897.47
8	887.36	887.35	887.35	887.35
11	901.56	901.54	901.54	901.54
12	897.01	897.01	896.99	896.99
19	890.49	890.47	890.46	890.46
12 FT PYRAMID PLUGS				
6	892.34	892.33	892.33	892.33
10	902.76	902.70	902.70	902.70
15 FT CONCRETE CAP				
1	901.90	901.90	901.90	901.90
13	895.12	895.09	895.08	895.08
BACK-FILLED ONLY				
14	898.21	897.95	[1]caved	[2]caved

[1] Caved 23 ft, estimated 125 yd^3 to reestablish to grade elevation.
[2] Caved 30 ft, estimated 150 yd^3 to reestablish to grade elevation.

All the closure devices remained stable for a period of 12 months (table 3). Subsidence was noticed around shaft No. 14 during a visit to the demonstration area 18 months after completion of the demonstration work. However, no subsidence was noted around any of the other shafts. Inspection of shaft No. 14 a month later and a resurvey of the reference monuments in October 1984 indicated that shaft No. 14 had caved 23 feet. It would require about 125 yd^3 of fill material to reestablish grade. The fill in shaft No. 14 has continued to subside. The survey completed Nov. 1986, indicated that the crater would require about 150 yd^3 of fill to reestablish grade. No appreciable movement of any of the other closure devices has been noted after 3 years of monitoring.

Shaft No. 14 was backfilled to locally established practice. It originally was to be the control reference to determine the success of closing the other 13 shafts. However, its sudden failure probably resulted from the failure of a temporary bridge that developed during the backfilling process or existed prior to backfilling. No effort had been made to remove trash from any of the shafts prior to backfilling or to determine whether there was pre-existing bridging. Nor was a bulkhead established at the base of the shaft to contain the shaft fill material and prevent it from spilling or being washed into the underground mine workings.

CONCLUSIONS

Eleven shafts were closed using the Bureau of Mines designed inverted pyramid-shaped concrete plugs. For comparison with more conventional backfilling, two shafts had a reinforced-concrete cap installed after backfilling and a third was simply backfilled. Initially, all of the three closure methods used in the demonstration project appeared to be effective methods for shaft closure in the Galena, KS, area. Survey data, table 3, compiled over a 3-year period indicate that only the 11 plugs and 2 caps were stable.

For the shallow shafts backfilling is probably a practical way to eliminate safety hazards. Backfilling of deeper shafts can require large amounts of fill material, particularly where large mine openings exist at the base of the shafts. For instance a 90-ft high opening at the base of a shaft can require up to 67,000 yds^3 of fill material to reach the base of the shaft. Further subsidence can continue to be a problem with backfilling.

For any shafts of any depth, either installing concrete caps or pyramid plugs is effective. The method selected depends to a great extent on the cost of labor. For either method, labor is cost intensive, due in part, to the restrictions of a safety harness while working within the abandoned mine shaft's potential collapse zone. The concrete caps required the most time exposure of personnel spent working over a mine shaft and required more concrete than the plugs for closing a given size shaft.

The inverted pyramid plug was the preferred method for closing the shafts in this demonstration project. This method was the easiest closure device to install and could easily be done assembly line fashion for closing a large number of shafts in a relatively short time. The plugs required the least amount of work in the immediate vicinity of a potentially dangerous abandoned mine shaft. The most time intensive installation step was spent in setting up the 17-ton crane, while avoiding locating it over any known underground workings, to safely place the plug forms in the shafts. Most of the labor was spent in fabricating the disposable forms. However, this was performed in a welding shop away from the demonstration site. Evaluation of the closure devices is being continued over a longer period of time to further prove their stability.

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